Organic Chemistry

Bernthesen

named section. The system of International Nomenclature agreed upon at the recent conference of chemists at Geneva has also been duly taken into account, both in the text of the methane derivatives and in the index, the "official name" being generally added in brackets to that hitherto in use.

Dr. Edward Buchner, of the University of Munich, has co-perated with me in bringing out this edition, and it is my leasant duty to thank him here for the resource and care of which he has given proof throughout the work. I should also ke to express my obligations to the many friends and col-agues who have shown their interest in the book by corre-ondence and by pointing out errors in the text, etc.

A. BERNTHSEN.

MANNHEIM, *June*, 1893.

AUTHOR'S PREFACE

TO THE FIRST GERMAN EDITION.

In lecturing upon Organic Chemistry in the University of Heidelberg, I have felt more and more each session the desirability of being able to place in the hands of my students a small text-book, which, while not exceeding some thirty sheets in size, and of which the descriptive portion was condensed as far as practicable, should yet be of a strictly scientific character; a book which, beginning with homologous series, should lay especial emphasis upon summarizing the characteristics of each class of compounds, and, wherever possible, upon the inductive development of the theoretical relations existing between them.

The following text-book of Organic Chemistry is an attempt to fulfil these requirements. Excepting in a few cases, where another arrangement appeared to be more suitable, there is given here for each class (after a short general description) a concise statement of the occurrence, general modes of formation, constitution and isomerides, and behaviour of the compounds in question. The choice of the compounds described has been practically determined by the requirements of teaching. A number of tables are incorporated, which I have already found useful in my lectures, and which are of service for summarizing.

The treatment of the theoretical matter is, especially in the first half of the book, purely inductive; the isomeric relations of the paraffins, for instance, are first referred to under butane,

and no constitutional formula of any important compound is given without the grounds for it being indicated. The inductive method is also retained even where, as in the case of the theory of the benzene derivatives, the historical development has run on other lines. In accordance with this the class definitions are based not on theoretical but on actual relations.

Type of two sizes has been employed in the book, in order that the matter which is of the greatest importance, either in itself or for the purposes of a general review, may be readily distinguished.

I have deemed it advisable to give a number of references with regard to points which have a particular historical value, and also to some of the more important recent researches, especially where space did not allow of these being treated in detail.

Special pains have been taken to make the index complete.

I trust, therefore, that the book will be found useful, not only to the student of chemistry proper on his entering upon the study of Organic Chemistry, but also to students of medicine and pharmacy, whose requirements have been carefully borne in mind. It should also prove of service to chemists engaged in technical work, who may wish to obtain a short survey of the present state of our science.

I should feel greatly obliged if my readers would kindly draw attention to any inaccuracies of statement or errors of print which may have crept into the work.

(Signed) A. BERNTHSEN.

HEIDELBERG, *April*, 1887.

ABBREVIATIONS

A. = Liebig's Annalen der Chemie.
Ann. Chim. Phys. = Annales de Chimie et de Physique.
Arch. f. Phys. = Archiv für Physiologie.
B. = Berichte der Deutschen Chemischen Gesellschaft.
Bull. Soc. Chim. = Bulletin de la Société Chimique, Paris.
Ch. Soc. J. = Journal of the Chemical Society.
Chem. News = Chemical News.
Chem. Ztg. = Chemiker-Zeitung, Cöthen.
J. pr. Ch. = Journal für Praktische Chemie.
Monats. f. Chemie = Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Proc. Chem. Soc. = Proceedings of the Chemical Society.
Rec. Tr. Ch. = Receuil des Travaux Chimiques des Pays Bas.
Z. Anal. Ch. = Zeitschrift für Analytische Chemie.
Z. phys. Chem. = Zeitschrift für physikalische Chemie.
Z. physiolog. Chem. = Zeitschrift für physiologische Chemie.
"O. N." = Official Name (agreed upon by International Congress).
n. or N. = Normal.
(°) or B. Pt. = Boiling Point.
[°] or M. Pt. = Melting Point.

ORGANIC CHEMISTRY.

INTRODUCTION.

Organic Chemistry is the Chemistry of the Carbon Compounds. Formerly those compounds which occur in the organic, *i.e.* the animal and vegetable, worlds were classed under Organic, and those which occur in the mineral world under Inorganic Chemistry, the first to adopt this arrangement having been *Léméry* in his Cours de Chimie (1675). After the recognition of the fact that all organic substances contain carbon, it was thought that the difference between organic and inorganic compounds could be explained by saying that the latter were capable of preparation in the laboratory, but the former only in the organism, under the influence of a particular force, the life force—vis vitalis—(*Berzelius*). But this assumption was rendered untenable when *Wöhler* in 1828 synthetically prepared urea, CON_2H_4, a typical secretion of the animal organism, from cyanic acid and ammonia, two compounds which were at that time held to be inorganic; and when, shortly afterwards, the synthesis of acetic acid, by the use of carbon, sulphur, chlorine, water and zinc, was effected.

Since then so many syntheses of this kind have been achieved as to prove beyond doubt that the same chemical forces act both in the organic and inorganic worlds.

The separation of the two branches, Organic and Inorganic Chemistry, from each other is, however, still retained for convenience sake, although the original reasons for this separation, which at the time was more or less a matter of necessity, have since been found to be erroneous. In consequence of the great capability for combination which carbon possesses, the number of organic compounds is extraordinarily large, and in order to

be in a position to study them, it is necessary to have a knowledge of the other elements, including the metals. The carbon compounds, many of the most important of which contain only carbon and hydrogen, or carbon, hydrogen, and oxygen, also stand in a closer relationship to each other than do the compounds of the other elements. Partly upon grounds of convenience, carbon itself and some of its principal compounds, such as carbonic acid, which is so widely distributed in the mineral kingdom, are treated of under Inorganic Chemistry.

One must not confound the terms "organic" and "organized" bodies; the latter, *e.g.* leaves, nerves and muscles, and also the life-processes which go on in the interior of the organism, are treated of under Physiology and Physiological Chemistry.

Constituents of the Carbon Compounds.

Many organic substances are made up of carbon and hydrogen alone, such being termed hydrocarbons, for instance, ethylene, benzine, petroleum, benzene, naphthalene, and oil of turpentine; a vast number consist of carbon, hydrogen, and oxygen, for instance, wood spirit, alcohol, glycerine, aldehyde, oil of bitter almonds, formic acid, acetic acid, stearic acid, tartaric acid, benzoic acid, carbolic acid, tannic acid, and alizarin; many (chiefly basic) compounds contain carbon, hydrogen, and nitrogen, for instance, prussic acid, aniline, and conine; as examples of compounds containing carbon, hydrogen, nitrogen, and oxygen, may be taken urea, uric acid, indigo, morphine, and quinine. In addition to these, sulphur, chlorine, bromine, iodine, phosphorus, and, generally speaking, the larger number of the more important elements, are also frequent constituents of the carbon compounds.

Qualitative Analysis of Organic Compounds.

The presence of **Carbon** in a compound is often proved by the "carbonization" of the latter, *e.g.* starch, sugar, &c., when heated in a glass tube, or when concentrated sulphuric acid is poured over it. Those compounds which boil without decom-

position deposit carbon when their vapours are led through a red-hot tube. But the best proof of the presence of carbon is obtained by completely oxidizing the organic compound by either heating it with copper oxide (see below), or by leading its vapour over the glowing oxide. The carbon present is thus converted into carbon dioxide, and the **Hydrogen** into water.

Nitrogen in organic compounds is recognized—

(*a*) Frequently by a smell resembling that of burnt hair, upon heating;

(*b*) Frequently by the presence of red fumes, or by explosion, upon heating (nitro- and diazo-compounds);

(*c*) In most cases by the liberation of ammonia upon heating with soda-lime (*Wöhler*);

(*d*) In all cases by heating with potassium (and in most cases with sodium), and testing the metallic cyanide formed —(see Cyanogen Compounds)—by dissolving the melted mass in water, adding alkali and a few drops of ferrous sulphate and ferric chloride solutions, boiling, and saturating with hydrochloric acid (formation of Prussian Blue); or by converting the cyanide into thiocyanate, and proving the presence of the latter by means of the blood-red coloration with ferric chloride. [See tests for hydrocyanic acid (*Lassaigne*).] If sulphur be likewise present, iron filings must be added.

Testing for the **Halogens**. Direct addition of nitrate of silver is usually not practicable; thus, no chlorine can be detected in chloroform even upon boiling it with $AgNO_3$. The halogens are therefore tested for:

(*a*) By heating the substance on a platinum wire with cupric oxide in the *Bunsen* flame, or by causing the vapour of the compound to pass over glowing copper gauze; in this way chlorine gives first a blue and then a green flame coloration, and iodine a green (*Beilstein*);

(*b*) By heating the substance strongly with pure lime, and testing the haloid calcium salt produced with silver nitrate,

(*c*) By heating in a sealed tube with fuming nitric acid and nitrate of silver, when the haloid silver salt is produced (*Carius*).

Testing for **Sulphur:**

(*a*) In many cases, upon boiling with an alkaline solution of lead oxide, brown sulphide of lead is formed (*e.g.* white of egg);

(*b*) By heating with sodium, and testing the resulting sodium sulphide with water upon a silver coin (black stain); or by means of sodium nitroprusside (purple-violet coloration) (*Schönn*);

(*c*) By complete oxidation in the dry way, by fusing with potassium hydrate and nitre, or by heating with mercuric oxide and sodic carbonate; or in the wet way, by fuming nitric acid (*Carius*), and testing the sulphuric acid produced, by chloride of barium.

In like manner **Phosphorus** is converted by complete oxidation into phosphoric acid; or, upon heating with powdered magnesia, and moistening the resulting mass with water, the presence of phosphuretted hydrogen can be recognized (*Schönn*).

All the **other Elements** are tested for, after complete oxidation of the compound (preferably by *Carius'* method), in the usual way.

Quantitative Organic or Elementary Analysis.

A. Estimation of Carbon and Hydrogen (Combustion). The substance is oxidized by heating it to redness with cupric oxide (*Liebig*), or with other substances which readily give up oxygen, such as lead chromate, platinum asbestos and oxygen (*Kopfer*), &c., in a tube of difficultly fusible glass, which is open either at one or at both ends.

The carbon dioxide, thus produced by the oxidation of the carbon, is absorbed by a moderately concentrated solution of caustic potash contained in specially shaped bulbs (*Liebig, Mohr, Mitscherlich, Winkler, Delisle, &c.*), and the water, produced by the oxidation of the hydrogen, in a U-shaped chloride of calcium tube, both tubes being weighed before and after the combustion. If the substance—(0·2 to 0·3 grm.)—is solid, it is either mixed with fine copper oxide (*Liebig, Bunsen*), or placed in a porcelain

or platinum boat and burnt in a stream of air or oxygen (open tube). Liquids are weighed out in small thin sealed glass bulbs. When nitrogen is present, a spiral of copper-foil is placed in the front part of the combustion tube and heated to redness, in order to reduce any oxides of nitrogen which may be formed in the subsequent combustion. In the presence of sulphur or of the halogens, lead chromate, which has been fused and then powdered, is used instead of copper oxide, so as to convert any Cl, SO_2, &c., into $Pb\,Cl_2$, $Pb\,SO_4$, &c., and so to prevent them from passing into the potash solution. When only halogens, without sulphur, are present, the combustion is carried out with copper oxide, a copper, or still better a silver spiral, which is kept cool, being placed in the fore-part of the tube to retain the halogens.

In the presence of alkalies or alkaline earths (which would retain carbon dioxide), lead chromate mixed with $\frac{1}{10}$th of its weight of potassic bichromate is used; the chromic acid then expels all the carbonic acid.

Explosive compounds must be burnt in a vacuum. From the weights of carbon dioxide and water found, the percentages of C and H are readily calculated:

$$C = \tfrac{3}{11}\,CO_2;\quad H = \tfrac{1}{9}\,H_2O.$$

B. Estimation of Nitrogen. This estimation is either relative or absolute. In the former case the proportion between the nitrogen and the carbonic acid evolved is determined (*Liebig, Bunsen*); in the latter the nitrogen is either estimated as such volumetrically, or as ammonia.

The conversion into **Ammonia** is effected by heating the substance strongly with soda-lime (*Will, Varrentrapp*), or by treating it with strong sulphuric acid and permanganate of potash (*Kjeldahl;* Z. Anal. Ch. 22. 366; also B. 19, R. 852; 24, 3241). The ammonia is then either titrated directly, or transformed into the double chloride of ammonium and platinum, $(NH_4Cl)_2\,PtCl_4$, which is then weighed, or else ignited, and the weight of the residual metallic platinum noted.

In the **Volumetric Estimation of Nitrogen** the substance is mixed with copper oxide, a copper spiral being also used, and the combustion is carried out in the usual way, but in a stream of carbonic acid; the CO_2 is either generated from magnesite in the tube itself, or led through it. The nitrogen is collected over mercury and aqueous caustic potash (*Dumas*), or directly over potash (*Zulkowsky*, *Schwarz*, *Schiff*, &c.).

Its percentage is got from the formula—

$$N \text{ (per cent.)} = V \cdot \frac{273}{273+t} \cdot \frac{b-w}{760} \cdot 0{\cdot}001256 \cdot \frac{100}{g}$$

where V = the volume of the nitrogen,
b = the barometric pressure
t = the temperature,
w = the tension of the water vapour,
0·001256 = the weight of a normal cubic centimeter of nitrogen,
and g = the weight of the substance taken.

The volumetric method is available in every case, but the other (ammonia) method not always; not, for instance, in the case of nitro-compounds, of many organic bases, &c., the nitrogen of these not being completely transformed into ammonia upon heating with soda-lime.

For the simultaneous determination of carbon, hydrogen, and nitrogen, the combustion must be carried on in a stream of pure oxygen, the mixture of gases escaping from the potash bulbs being collected over a solution of chromous chloride, which absorbs the oxygen but not the nitrogen (A. 233, 375).

C. Estimation of Sulphur and Phosphorus. The Sulphur is estimated as sulphuric acid, being converted into this—

(*a*) in the wet way, by heating the substance with fuming nitric acid to 150°–300° in a sealed tube (*Carius*), or in a combustion tube in a mixed stream of nitric oxide and oxygen (*Claësson*), or nitric acid vapour (*Klason*).

(*b*) in the dry way—(and this method is only available in the case of the less volatile compounds)—by fusing the substance with potassic hydrate and nitre, or with soda and

chlorate or chromate of potash, also by heating with soda and mercuric oxide, or with lime in a stream of oxygen, and so on;

(c) by burning in a stream of oxygen and collecting the SO_2 formed in hydrochloric acid containing bromine (*Sauer;* cf. Z. Anal. Ch. **12**, 32, 178).

Phosphorus is estimated by analogous methods.

D. Estimation of the Halogens. Here also the organic substance is completely decomposed—

(*a*) after *Carius*, as above, in a sealed tube, with addition of silver nitrate, by which means the halogen is converted into its silver salt;

(*b*) by heating the compound strongly with pure lime in a hard glass tube, or in two crucibles, one of which is inverted in the other, or with sodic carbonate and nitre in a tube. The chloride formed is precipitated with silver nitrate in the usual way;

(*c*) by the action of nascent hydrogen (sodium amalgam), the halogen in the organic substance can frequently be converted into its hydrogen compound (*Kekulé*).

E. Inorganic Bases and Acids, contained in organic salts, can often be estimated directly by the usual methods.

F. Oxygen is almost invariably determined by difference; direct methods of estimation have been proposed by *Baumhauer*, *Ladenburg*, *Stromeyer*, and others.

The limit of error in an estimation of carbon is about 0·05 to 0·1 p.c., in one of hydrogen +0·1 to 0·2 p.c., while in the volumetric estimation of nitrogen several tenths p.c. too much are easily found.

The Calculation of the Formula.

The same principle applies here as in the case of inorganic compounds, *i.e.* the percentage numbers found are divided by the atomic weights of the respective elements, the relative proportions of the quotients obtained being expressed in whole numbers. For instance, acetic acid being found to contain 40·11 p.c. carbon, 6·80 p.c. hydrogen, and, consequently, 53·09

p.c. oxygen, the quotients are to each other as 3·34 : 6·80 : 3·32 = 1 : 2 : 1. The simplest analysis-formula of acetic acid would therefore be CH_2O. Sometimes figures are obtained which correspond with equal nearness to different formulæ, between which it is therefore impossible, without further data, to choose.

For instance, a sample of naphthalene yields on analysis 93·70 p.c. carbon and 6·30 p.c. hydrogen; the quotient proportion here is 7·81 to 6·30 = 1·239 : 1, which corresponds equally well with the numbers 5 : 4 or 11 : 9. The formula C_5H_4 requires 93·75 p.c. carbon and 6·25 p.c. hydrogen, and the formula $C_{11}H_9$, 93·62 p.c. carbon and 6·38 p.c. hydrogen, the deviations from the actual numbers found being in both cases within the limits of experimental error. Therefore other considerations must be taken into account here, in order to decide between the two formulæ.

Even in simple cases, such as that of acetic acid, the formula found (CH_2O) is not to be taken as the molecular formula without further proof; it only expresses the atomic number proportions. The molecular formula has to be determined according to special principles.

Determination of Molecular Weight.

1. By Chemical Methods.

Our chemical formulæ (*e.g.* CH_2O) express not merely a percentage relation, but at the same time the smallest quantity of the compound which is capable of existing as such, *i.e.* a molecule of it. This molecule is ideally no longer divisible by mechanical means, but only by chemical, and then into its constituent atoms. If the formula CH_2O were the correct one for acetic acid, then the amount of oxygen (or carbon) contained in a molecule would be indivisible, and that of hydrogen divisible only by 2. Since, however, it has been observed that one-fourth of the total hydrogen in acetic acid is replaceable, *e.g.* by a metal, with the formation of a salt, it is obvious that the quantity of hydrogen in the molecule must be divisible by 4, and so the formula must contain at least 4 atoms of hydrogen, and must therefore be $C_2H_4O_2$, or some multiple of it. This is, in fact, the case. Acetate of silver contains 64·67 p.c. silver, and therefore 35·33 p.c. of the acetic acid radicle; or, to 1 atom of silver = 108 parts by weight, there are 59 parts by weight of the acid radicle. This 59, together with 1 atom of hydrogen = 1,

makes the molecular weight of acetic acid 60, $= 2 \times 30$, $= 2 \times CH_2O$, $= C_2H_4O_2$.

This is a determination of molecular weight by **chemical means.** Such determinations are carried out in the case of acids generally by means of their silver salts, which are usually constituted normally, are easy to purify, are almost always free from water of crystallization, and are readily analysed. One only requires to know here whether the acid is mono- or polybasic. In the case of a di-, tri-, &c., basic acid, the above calculation must be made with reference to 2, 3, &c., atoms of silver, whereas acetic acid—being monobasic—contains only one replaceable atom of hydrogen, which is therefore exchanged for one atom of silver. Consequently, its formula cannot be a multiple of $C_2H_4O_2$.

In the determination of the molecular weight of **Bases**, their platinum salts are similarly made use of, these being almost always constituted on the type of platinum-ammonium chloride: $(NH_4Cl)_2, PtCl_4$: *i.e.* they contain two molecules of hydrochloric acid and one molecule platinic chloride to every two molecules of a mono-acid, or to one molecule of a di-acid base.

To determine the molecular weight of **Indifferent Compounds**, derivatives must be prepared and examined for the proportion of the total hydrogen which is replaceable, *e.g.*, by chlorine. For example, by the action of chlorine upon naphthalene, there is first formed the substance mono-chloro-naphthalene, which contains 73·8 per cent. C, 4·3 per cent. H, and 21·9 per cent. Cl, these numbers giving the formula $C_{10}H_7Cl$. In the same way benzene yields the compound C_6H_5Cl. In both these cases the halogen acts by replacing hydrogen, and at least one atom of the latter in the molecule must be replaced, since fractions of an atom are necessarily out of the question. If, then, the compound obtained has the formula $C_{10}H_7Cl$, it follows that $\frac{1}{8}$th of the H present has been replaced by Cl, and there must consequently be 8, 8×2, or 8×3, &c., atoms of hydrogen in the compound, and likewise 10 atoms, or some multiple of 10, of carbon. But a multiple of 8 or 10 may be rejected, since no compounds have been observed which would

indicate the replacement of $\frac{1}{8}$th of the total hydrogen. This leads to the formula $C_{10}H_8$ for naphthalene, the other possible formula got by analysis, viz., $C_{11}H_9$ (see p. 8), being now untenable. In a similar way the formula of benzene is found to be C_6H_6.

2. By Physical Methods.

a. *By Estimating the Vapour Density.*

According to the law of *Avogadro* (1811), and *Ampère* (1814), all gases under similar conditions, *i.e.* in the perfectly gaseous state and under the same temperature and pressure, contain in equal volumes equal numbers of molecules. It follows from this that the weights of equal volumes of different gases are proportional to the weights of equal numbers of their constituent molecules, in other words, the molecular weight is proportional to the specific gravity of the gas. Thus, if M_x be the molecular weight of any given substance required, M_H that of hydrogen, S the specific gravity of the former as compared with air, and 0·06926 the corresponding specific gravity of the latter, then

$$M_x : M_H = S : 0{\cdot}06926.$$

And since $M_H = 2$,

$$M_x = \frac{2 \,.\, S}{0{\cdot}06926} = S \,.\, 28{\cdot}87.$$

To determine, therefore, the molecular weight of a gas, one has only to find its specific gravity, (air = 1), and to multiply this by 28·87.

To take an example, the specific gravity of acetic acid vapour being found to be 2·078, then

$$M = 2{\cdot}078 \times 28{\cdot}87 = 60,$$

and the molecular formula is $C_2H_4O_2 = 60$.

In like manner, the specific gravity of naphthalene vapour is 4·33 and the molecular weight $128 = C_{10}H_8$; the specific gravity of benzene vapour 2·702 and the molecular weight $78 = C_6H_6$.

It is essential to the application of this method that the temperature of the vapour shall be so high above the boiling

temperature of the substance that the latter is in the perfectly gaseous state, remaining at the same time undecomposed.

Up to a few years ago, the determination of molecular weight by physical means was restricted to the (different modifications of the) method which has just been described, and consequently it could only be carried out with substances which were either already gaseous, or which could be rendered so without decomposition.

The recent important researches of *van 't Hoff*, *Raoult*, *Arrhenius*, *Ostwald* and others, upon the nature of solution—in particular, the proof that the laws of *Boyle*, *Gay-Lussac* and *Avogadro* are applicable to solutions as well as to gases—now permit, however, of the ready determination of the molecular weight of substances in solution, and therefore of *compounds which could not be volatilized without decomposition.* This is accomplished as follows:—

b. *By Measuring the Depression of the Freezing Temperature of Solutions.*

According to *Raoult* (Ann. Chim. Phys., 1883 *et seq.*), the law holds that "*Equimolecular solutions have the same point of solidification.*" By equimolecular solutions are meant such as contain, in equal quantities of the solvent, quantities of the dissolved substances proportional to their molecular weights.

If n molecular weights in grammes of a substance are dissolved in g grammes of a solvent, and if the depression of the freezing point of that solvent is represented by Δ, then

$$\Delta = r . \frac{n}{g},$$

r being a constant, dependent upon the nature of the solvent alone.

This latter constant is first ascertained by dissolving compounds of known molecular weight in the solvent, and noting the depression produced. This gives—

$$r = \frac{\Delta g}{n}.$$

In order now to determine the (unknown) molecular weight m of another compound, p grammes of the latter are dissolved in g grammes of the solvent, and the freezing temperature of this solution is observed. We then have:— $n = \frac{p}{m}$;

and, consequently, $\Delta = \frac{rp}{mg}$, or $m = \frac{rp}{\Delta g}$.

Glacial acetic acid is of especial use as a solvent, but other substances are also employed, *e.g.* benzene, naphthalene, etc.

Cf. *V. Meyer*, B. **21**, 536 *et seq.*; also, for the apparatus employed, *Beckmann*, Z. Phys. Chem. **2**, 638 and 715; **7**, 323; **8**, 223; cf. also B. **25**, Ref. 265. The method can also be employed in many cases to study the course of a reaction (B. **25**. 1847).

c. *By Measurement of the Osmotic Pressure.*

According to *van 't Hoff* (Z. Phys. Chem. I. 481), all solutions which contain substances dissolved in the proportions of their molecular weights (*i.e.* in "equimolecular quantities") exert the same osmotic pressure, equality of temperature being assumed here. From this it follows, by reasoning analogous to that in section (b), that the molecular weight of a compound can be ascertained by measuring the osmotic pressure of its solution. (Cf. *Ladenburg*, B. **22**, 1225; *M. Planck*, Z. Phys. Chem. VI. 187.)

d. *By Measurement of the Lowering of the Vapour Pressure.*

According to *Raoult*, if molecular quantities of any given substances are dissolved in the same solvent, they give rise to an equal and constant lowering of the vapour pressure. This law can be deduced theoretically from the preceding one (c), and it also stands in theoretical continuity with that of (b). For its application to the determination of molecular weights, cf. Z. Phys. Chem. **2**, 353, 602; **3**, 603; **4**, 532; **6**, 437; B. **22**, 1084. In the journal last quoted the literature on the subject is given.

e. *By Measuring the Decrease in Solubility.*

(*Nernst*, B. **23**, Ref. 619.)

Appendix: Determination of the Specific Gravity of Gases and Vapours. (Vapour Density.)

A. By estimating the weight of a given volume of the gas or vapour.

1. *Bunsen's* method. Three glass balloons of equal size and weight are used, the first being pumped empty of air, and the second and third filled respectively with air and with the gas in question in a thermostat at a constant temperature. The respective weights of the balloons being p_1, p_2 and p_3, the specific gravity $= \frac{p_3 - p_1}{p_2 - p_1}$

2. *Dumas'* method. 10 to 20 grm. of the substance are heated to boiling in a round glass balloon with a narrow neck, immersed, *e.g.*, in an oil-bath. After the temperature has remained constant for a considerable time, the point of the neck is closed by the blowpipe, and the balloon weighed; it is then opened over mercury and weighed again.

Both of the above methods require a large quantity of material and, further, if the substance be not absolutely pure, the last-mentioned method will be liable to the error caused by the vapour of the more difficultly volatile constituent remaining in large quantity in the balloon. *Troost* and *Hautefeuille* have modified the method for higher temperatures, using a porcelain balloon.

B. By estimating the volume of vapour from a given weight of substance.

1[a]. *Gay Lussac's* method. The substance, weighed in a small bulb, is introduced into a glass cylinder filled with mercury. This cylinder is surrounded by a glass mantle, the lower end of which also dips into mercury, and which is filled with a hot liquid, such as water, aniline, etc. The whole apparatus is warmed and, after the substance in question has been completely vaporized, its volume at the temperature $t°$ is determined.

1[b]. *A. W. Hofmann's* method. The substance is introduced into a barometer tube surrounded by a wider cylinder, through which the vapour of a suitable heating liquid (water, aniline, diphenylamine, etc.) is led. The cylinder can itself act as a reflux condenser.

One advantage of this method is that, by the use of a partial or even complete vacuum, the boiling point of the substance in question is lowered, and thus the vapour density of compounds which decompose on being gasified under the ordinary atmospheric pressure can be determined. There are various modifications of this most accurate method.

2. *V. Meyer's* air-displacement method. The small tube containing the substance is dropped into a vertical glass tube, the lower and wider part of which is cylindrically shaped and sealed. This is kept warm at a constant temperature, being surrounded by a long glass mantle in which a suitable liquid boils, the upper part of the mantle itself serving for the condensation of the vapour. The displaced air alone escapes, and is collected over water and measured. No determination, therefore, of the temperature of the vapour of the substance in question is required. Both of the above methods require only up to 0·1 grm. substance. In all cases

$$S = \frac{g}{v}$$

where g = the weight of the vapour, and v = the weight of an equal volume of air.

Thus by the air-displacement method

$$S = \frac{g}{n\frac{(b-w)}{760} \times \frac{273}{273+t} \times \frac{1}{773}}$$

where n = the number of cubic centimetres of displaced air, 1 c.c. of air at 0° C. and 760 m.m. pressure weighing $\frac{1}{773}$ of a gramme. The other figures have the same meaning as on p. 6.

If, instead of having the apparatus filled with air, hydrogen is employed, the greater molecular velocity of the latter allows of the conversion of substances into vapour at 30°–40° below their ordinary boiling temperatures (*V. Meyer* and *Demuth*, B. 23, 311)

Polymerism and Isomerism.

The determination of molecular weight is of the first importance, because different substances very frequently have the same percentage composition and therefore the same empirical analysis-formula, and yet are totally distinct from one another. This difference is often found to arise from difference in the size of the molecule. Thus formic aldehyde, CH_2O, acetic acid, $C_2H_4O_2$, lactic acid, $C_3H_6O_3$, and grape sugar, $C_6H_{12}O_6$, have all the same percentage composition, as have also ethylene, C_2H_4, propylene, C_3H_6, and butylene, C_4H_8. Compounds standing in such relation to each other are termed **polymers.** Very frequently, however, substances which are totally distinct from each other possess both the same percentage composition and the same molecular weight; that is to say, these compounds are made up not only of the same atoms, but also of an equal number of these atoms; such substances are termed **isomers** or **metamers.** (See Ethers.) Thus, for instance, common alcohol and methyl ether, the latter of which is obtained by heating methyl alcohol with sulphuric acid, have one and the same molecular formula, C_2H_6O.

The striking phenomenon of isomerism is only explicable on the assumption that the grouping of the constituent atoms of the molecule is different in the two cases. This difference in grouping may be considered as being due to a difference in the linking powers of the atoms, as is indicated by the dissimilar chemical behaviour of isomers, and explained by the theory of valency. See p. 17.

Chemical Theories; the Theory of Valency.

After the fall of the Electro-Chemical theory, unitary formulae—in contradistinction to the earlier dualistic formulae—were much used; thus alcohol had the formula $C_4H_6O_2$ (using the old equivalent weights). The necessity for comparing substances of complicated composition with simpler ones, taken as "Types," had already repeatedly led to the propounding of new theories for representing the constitution of organic compounds, *e.g.* the older Type theory (*Dumas*), and the Nucleus theory (*Laurent*).

These obtained a firmer basis through *Gerhardt's* **Theory of Types**, which received support more especially from the discovery of ethylamine and other ammonia bases [*Wurtz* (1849) and *Hofmann* (1849, 1850)], the proper interpretation of the formulae of the ethers [*Williamson* (1850)], and the discovery of the acid anhydrides [*Gerhardt* (1851)]. All compounds, inorganic as well as organic, were in this way compared with simpler inorganic substances taken as "**Types**," of which *Gerhardt* named four, viz.—

$$\left.\begin{matrix}H\\H\end{matrix}\right\}\qquad\left.\begin{matrix}H\\Cl\end{matrix}\right\}\qquad\left.\begin{matrix}H\\H\end{matrix}\right\}O\qquad\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$$

The first two of these really belong to the same type. Thus the following formulae, for example, were arrived at—

$$\left.\begin{matrix}H\\Cl\end{matrix}\right\}\qquad\left.\begin{matrix}K\\Cl\end{matrix}\right\}\qquad\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}\qquad\left.\begin{matrix}C_2H_3O\\Cl\end{matrix}\right\}$$

Potassium chloride. Ethyl chloride. Acetyl chloride.

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O\qquad\left.\begin{matrix}K\\H\end{matrix}\right\}O\qquad\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O\qquad\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O\qquad\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$$

Potassium hydrate. Nitric acid. Alcohol. Acetic acid.

$$\left.\begin{matrix}K\\K\end{matrix}\right\}O\qquad\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O\qquad\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O\qquad\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O$$

Potassium oxide. Nitric anhydride. Ether. Acetic anhydride.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\qquad\qquad\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N\qquad\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$$

Ethylamine. Acetamide.

etc., etc. Organic compounds could thus, like inorganic, be referred to inorganic types by assuming in them the presence of Radicles (*e.g.* ethyl, C_2H_5; acetyl, C_2H_3O, etc.), *i.e.* of groups of atoms which play a part analogous to that of an element, and which can be transferred by double decomposition from one compound to another. Thus ethyl chloride, C_2H_5Cl, alcohol, C_2H_6O, ethylamine, C_2H_7N, ether, $C_4H_{10}O$, etc., received the same radicle C_2H_5, ethyl, this showing the close relationship existing between these compounds, a relationship which now found in this way expression in writing.

Sulphuric acid, H_2SO_4, was derived from the double water type, thus—

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2\qquad\qquad\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2\,;$$

and chloroform, $CHCl_3$, and glycerin, $C_3H_8O_3$, from the triple hydrochloric acid and water types—

$$\left.\begin{matrix}H_3\\Cl_3\end{matrix}\right\}\qquad\left.\begin{matrix}(CH)'''\\Cl_3\end{matrix}\right\}\,;\qquad\qquad\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3\qquad\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3\,;$$

the assumption being made that the radicles $(C_2H_5)'$, $(SO_2)''$, $(CH)'''$, and

$(C_3H_5)'''$ could replace a number of hydrogen atoms corresponding to the number of accents (′) marked upon them, *i.e.* that they were monatomic, diatomic, etc. To the above three types *Kekulé* afterwards added a fourth, of especial importance as regards the carbon compounds, viz.—

$$\left.\begin{array}{l}H\\H\\H\\H\end{array}\right\}C\text{, Marsh gas.}$$

It was then found that many compounds could be referred equally well to one or another of these types, methylamine, for instance, either to CH_4 or to NH_3, thus—

$$\left.\begin{array}{l}NH_2\\H\\H\\H\end{array}\right\}C \quad \text{or} \quad \left.\begin{array}{l}CH_3\\H\\H\end{array}\right\}N.$$

The assumption, already mentioned, of the atomic groups (radicles) which in these types replaced hydrogen, led further to more exact investigations of the chemical value, *i.e.* the replaceable value, of those groups as compared with that of hydrogen. In this way chemists learnt to distinguish between mono-, di-, tri-, etc., valent groups, and, generally speaking, to pay more attention to equivalent proportions.

As the outcome of his researches upon organo-metallic compounds, *Frankland* formulated in 1852 (A. **85**, 368) the law that the elements nitrogen, phosphorus, arsenic and antimony tend to form compounds which contain three or five equivalents of other elements.

Kekulé then, in 1857–8 (A. **104**, 129; **106**, 129), proceeded to show that a more profound idea (the "Type idea") lay at the root of the types themselves, viz., that there are mono-, di-, tri-, and tetravalent, etc., elements, which possess a corresponding replacing or combining value as regards hydrogen; and that hydrogen is therefore monovalent, oxygen divalent, nitrogen trivalent, carbon tetravalent, and so on.

The principles of the theory of Valency or theory of Chemical Values are in this book assumed to have been already learnt from inorganic chemistry.

With the setting up of the type CH_4 by *Kekulé*, and the knowledge of the tetravalent nature of carbon accompanying this, were connected the endeavours of *Kolbe* to derive the constitution of organic compounds from carbonic acid (according to *Kolbe* C_2O_4, $C=6$, $O=8$), by the exchange of oxygen for organic radicles (A. **113**, 293); see also, for further details, *Kopp's* "Entwickelung der Chemie in der neueren Zeit" (Oldenbourg, Munich, 1873), and *E. V. Meyer's* "History of Chemistry" (Macmillan, 1891).

The question of the valency of elements, a point which it is often difficult to decide in inorganic chemistry, is infinitely easier of determination in the case of the carbon compounds, because carbon shows itself tetravalent towards hydrogen as well as towards chlorine and oxygen. Since now hydrogen as the unit of valency is monovalent, and, further, since the divalence of oxygen cannot reasonably be doubted, the valency of the three "organic" elements hydrogen, oxygen and carbon may be considered as resting upon a sure basis, as may also the

conclusions drawn therefrom, and this all the more since the most important carbon compounds are made up of those three elements.

Explanation of Isomerism; Determination of the Constitution of Organic Compounds.

The theory of valency makes the phenomenon of Isomerism easy to understand. That this depends upon the different grouping or combination of the atoms in the molecule follows from the fact that isomeric bodies, upon chemical transformation, break up into or exchange perfectly different atomic groups or atoms.

We now arrive at the task of determining the different modes of combination of the atoms in the molecule, *i.e.* the **chemical constitution** of the carbon compounds.

This is in every case only possible and admissible for compounds whose chemical behaviour in the most dissimilar directions is known.

In considering this, let us fix our attention, in the first instance, upon the mode of linking of atoms in a molecule which can be subjected to the test of actual experiment, leaving aside the further point as to how far a difference in the grouping of atoms in space may come into question here. With regard to this latter, see p. 21 *et seq.*

The points of view which determine this can best be explained by giving an example. When an ethereal solution of methyl iodide, CH_3I, is treated with sodium, there is first formed the group CH_3, methyl, which—from carbon being tetravalent—must have a "free affinity" (*)—

$$*—C\begin{matrix}/H\\—H\\\backslash H\end{matrix}$$

The determination of the molecular weight of the gaseous compound ethane, formerly called methyl, which is thus produced, shows however that it has the formula C_2H_6, $(=2CH_3)$. The two methyl groups have therefore combined together, and it cannot well be doubted that this combination is effected by their free affinities. Ethane therefore receives the constitutional formula—

$$H_3C—CH_3; = \begin{matrix}C\equiv H_3\\|\\C\equiv H_3\end{matrix};$$

or, more shortly,

$$\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} \text{ or } \left(\begin{array}{c} CH_3 \\ \cdot \\ CH_3 \end{array}\right).$$

This ethane can also be prepared from common alcohol. By the action of a halogen-hydride upon alcohol, one atom of oxygen and one of hydrogen together are exchanged for an atom of the halogen with formation, for example, of C_2H_5Cl, ethyl chloride; then nascent hydrogen, acting upon this chloride, replaces the halogen, thus,

$$C_2H_6O + HCl = C_2H_5Cl + H_2O\ ;$$
$$C_2H_5Cl + H_2 = C_2H_6 + HCl.$$

Conversely, by treating ethane with chlorine, ethyl chloride, C_2H_5Cl, can be formed, and from this latter compound, alcohol. (See Special Part.) Thus, one atom of oxygen and one of hydrogen have here replaced one atom of chlorine, from which it follows that the two first-named together form the monovalent residue—(O—H), hydroxyl. It is also evident from this reaction that one atom of hydrogen in alcohol behaves differently to the other five, and must consequently be differently bound. Thus it is, for instance, replaceable by metals, acid radicles, etc., and, when the oxygen is removed from the compound, it is removed also, whereas the other five hydrogen atoms are not affected. It is especially to be noted that the relation of the two carbon atoms to one another is not altered by the removal of the oxygen.

All these facts lead to the constitutional formula for alcohol:

$$CH_3—CH_2OH \text{ or } \begin{array}{l} C\equiv H_3 \\ | \\ |\diagup H. \\ C—H \\ \ \diagdown O—H \end{array}$$

In methyl ether, C_2H_6O, which is isomeric with this alcohol, no one of the six hydrogen atoms shows any difference to the others; and, further, when its oxygen is removed, say by the action of hydriodic acid, the connection between its two carbon atoms is broken, with the formation of products which contain

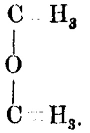
only one atom of carbon in the molecule, these products being, according to the conditions,—either one molecule methyl iodide and one molecule methyl alcohol or two molecules methyl iodide, thus—

$$C_2H_6O + HI = CH_4O + CH_3I,$$

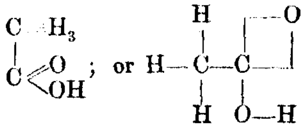
or,

$$C_2H_6O + 2HI = 2CH_3I + H_2O.$$

From this it is to be concluded that in methyl ether the two carbon atoms are not bound directly to one another, but only by interposition of the oxygen; so that when the source of this connection is removed, the carbon atoms separate from one another. These conditions find expression in the following constitutional (or structural) formula—

$CH_3—O—CH_3$; or 

In a precisely analogous manner we obtain for acetic acid the constitutional formula—



The grounds for this formula will be explained later on. It corresponds perfectly with the chemical behaviour of acetic acid and explains the following facts:—(*a*) that one of the hydrogen atoms of the acid possesses properties different to those of the three others, the first-named being easily replaceable by metals; (*b*) that the two oxygen atoms behave differently, not being exchangeable with equal ease for other elements or atomic groups; (*c*) that different functions appertain to the two carbon atoms, so that one of them—being already joined to two atoms of oxygen—easily gives rise to carbonic acid, while the other—connected as it is with three atoms of hydrogen—readily passes into methane or methyl compounds.

On account of the innumerable cases of isomerism which have been observed, empirical formulae alone are in most cases

insufficient for the discrimination of organic compounds; it generally requires the constitutional formulae to give a clear idea of their behaviour and of their relations to other substances. Careful study has made it possible within the last few decades to find out the mode in which the atoms are combined in the molecule of most organic compounds, and from this to deduce new methods for their preparation. The constitutional formulae thus arrived at are sometimes very simple, sometimes, however, very complicated, as, for instance, in the cases of citric acid and grape sugar (which see).

THE NATURE OF CARBON.

The theoretical views and the knowledge thereby gained of the nature of carbon may be expressed somewhat as follows:—

1. Carbon is tetravalent.

2. Its four valencies are all equal; there is only one mono-substitution product of methane.

3. The atoms or atomic groups which are held bound by these four valencies cannot directly exchange places with each other (the *Le Bel-van 't Hoff* law, 1874). Proof: there are in every case two physically different tetra-substitution products, C, a, b, c, d of methane (see p. 22).

4. Several carbon atoms can be connected together by either one, two, or three valencies (see p. 30): C—C, C=C, C≡C.

5. Similarly, three or more carbon atoms may be united, forming in this way the so-called "carbon chains" (see p. 29), thus—

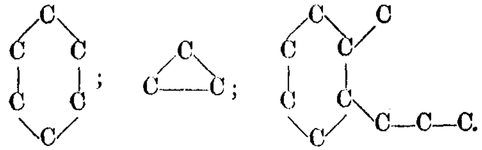
C—C—C—C; C—C—C=C—C—C; C≡C, C>C—C.

The number of the atoms so linked together may be a very large one, *e.g.* much above 30.

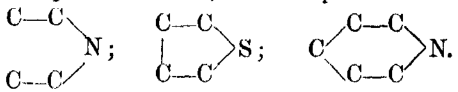
6. Those compounds form either open or ring-shaped closed chains.

Open chains are those which have separate constituent atoms at either end, as in (5). In *closed chains* or *atomic rings*, on the contrary, the first and last constituent atoms are linked

together (although there may at the same time be subsidiary branches from them), thus—



7. Other elements, with the exception, of course, of monovalent ones, may likewise take part in the formation of such chains, both open and closed; for example:—



The above figures (the hexagon, etc.), which are made use of to represent such chains or rings, are merely meant to be pictorial (*schematisch*) and not geometrical; the question of the spacial arrangement of atoms in compounds will be treated of later.

8. When a carbon atom is linked to four other atoms or atomic groups similar to each other, its four affinities apparently act uniformly and equally, as may be pictured in a regular tetrahedron whose central point is joined to each corner by straight lines. We may thus imagine the system (spacially) as a regular tetrahedron, the centre of which is occupied by the carbon atom, and in whose corners the centres of gravity of the four other atoms (etc.) are to be found.

If the four atoms (etc.) which are linked to the carbon atom be dissimilar, then the affinity-directions (*Affinitätsrichtungen*) will undergo corresponding diversions, the distances of the centres of gravity of the four atoms from the carbon atom will be different, and the whole system will give a picture of a less regular tetrahedron. (For further details, see under "Stereo-chemical Isomerism").

9. For the spacial distribution of valencies, and for an attempt to explain tension phenomena when carbon atoms are linked together by two or more bonds, cf. *Baeyer*, B. **18**, 2277.

STEREO-CHEMICAL ISOMERISM.

In the course of the investigation of the constitution of organic compounds, a variety of cases have gradually come to

light in which *the same constitutional formula must be given to two or more compounds*, seeing that they show a perfectly similar chemical behaviour, or at least a behaviour similar in many respects. Substances of this kind also frequently agree or closely resemble one another in their physical properties, and the one modification can usually be transformed into the other by very simple means, *e.g.* by raising the temperature (*i.e.* a "molecular transformation" is brought about).

It is the development of the above assumptions with respect to the spacial configuration of the carbon compounds which has led to a conception of the cause of such cases of fine isomerism. This latter is to be sought for in the relative spacial arrangement of the individual atoms within the molecule, *i.e. in the configuration of the molecule;* it is therefore termed *Stereo-chemical Isomerism*, or, less frequently, *Allo-isomerism.*

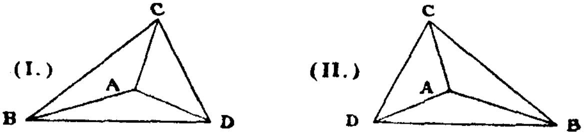
The above views were first published by *van 't Hoff*, and they have been developed, more particularly, by *J. Wislicenus.*

Cf. *van 't Hoff*, "Dix Années dans l'histoire d'une Theorie;" Rotterdam, 1887 (English translation by J. E. Marsh, Clarendon Press, 1891); *J. Wislicenus*, "Räumliche Anordnung der Atome," Leipzig (Hirzel), 1887; *ibid.*, B. **20**, Ref. 448; A. **248**, 281 *et seq.; Baeyer*, B. **18**, 2277; A. **245**, 103; *Auwers* and *Victor Meyer*, B. **21**, 784, 946; *V. Meyer*, B. **21**, 265, 288, etc.

Shortly stated, they are somewhat as follows:—

1. If *one* carbon atom is linked to four other atoms or atomic groups which differ from one another, *i.e.* if the carbon atom is "asymmetric," then only one constitutional formula is possible; an isomerism in virtue of different constitution is not conceivable. Nevertheless, two physically different tetra-substitution products of this kind may exist [see p. 20 (3)]. Thus, if we picture them as tetrahedra projected on the surface of this paper, the centre of each being occupied by the carbon atom, we shall get the two following configurations. (The carbon atom in the centre is not shown in the drawing; the linked atoms or atomic groups are designated by the letters A, B, C and D.)

The two figures below are not congruent, the one being the mirror image of the other. The succession of B, C and D is,



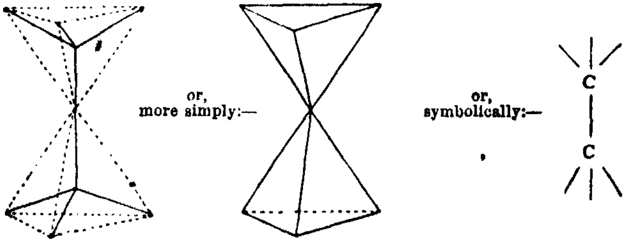
in the first case, in the same direction as the motion of the hands of a watch, while in the second it is just the opposite.

If, therefore, any physical property be dependent upon the spacial arrangement of these atoms or atomic groups, B, C and D, *e.g.* the power of optical rotation (see p. 38), then this property will be exercised in opposite directions in the two cases; if the compound which corresponds to fig. (I.) be dextro-rotatory, then the other will be laevo-rotatory; and so on.

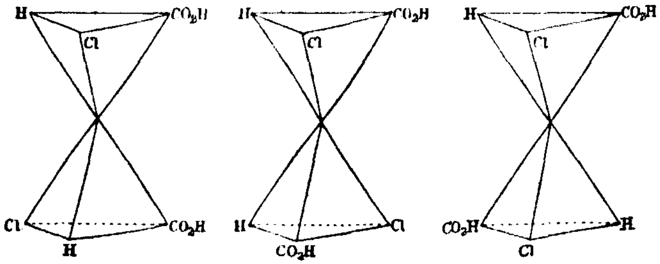
A simple explanation is thus afforded of the existence of isomeric compounds which differ from one another in their optical properties alone. For further details on this point, see under lactic acid.

2. If two carbon atoms are linked together by one affinity of each, and if they are at the same time asymmetric, the conditions which have just been described under (1) may repeat themselves in a variety of ways (see under tartaric acid).

Two carbon atoms, bound together by one affinity of each, may be thus represented:—



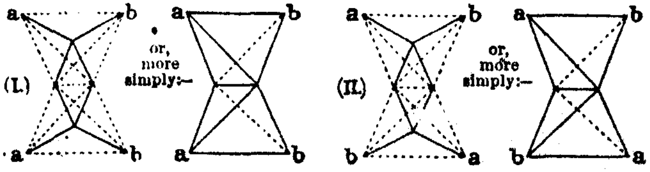
In general we have to assume in this case that the two atoms can rotate about their common axis independently of one another. At the same time the atoms which are linked to the one carbon atom will exert a discriminating (*orientirende*) action upon those which are linked to the other, according to the measure of their mutual attraction, in consequence of which they will take up a so-called "favoured" position. Supposing the groups H, Cl and CO_2H to be severally linked to both the carbon atoms, as is the case in dichlorosuccinic acid, CO_2H-CHCl-CHCl-CO_2H; then, taking the order of succession of the substituents as that just given (apart from intermediate positions), three configurations are possible, viz.:—



The strong affinity between hydrogen and chlorine, however, makes the first of those configurations the "favoured" one, and therefore the one which must recur most frequently.

It is further possible that the directive influences of these last-mentioned forces of attraction may even entirely arrest free rotation in certain cases. But no instances of this nature are as yet known with certainty.

3. If two carbon atoms are linked together by two affinities of each, then the system no longer possesses freedom of motion. Supposing that to each of the carbon atoms two different atoms or atomic groups, *a* and *b*, are united, then—with the same linking chemically—two isomers may exist, from the different distribution of *a* and *b*, thus (in the first and third figures the edges of the tetrahedra are merely indicated by dotted lines, the full lines showing the affinity-directions):—



or, abbreviated:—

(I.) *a*—C—*b*
    ||
  a—C—*b*

(II.) *a*—C—*b*
    ||
  b—C—*a*

In fig. I. *aa* stand in a "corresponding" or "plano symmetric" ("Γ cis") position to one another; in fig. II. in a "centrical-symmetric" or "axial-symmetric" ("Γ cistrans"). (I.) is therefore designated the "cis" form, seeing that in it both of the atoms or atomic groups *aa* are on one side of the plane which is formed by the affinity-directions of the double linking; (II.), on the other hand, is the "trans" form, *aa* being on opposite sides here.

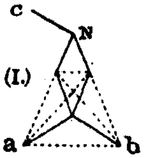
It is easy to imagine that in the one case the atoms or groups, *a* and *b*, would exert a stronger mutual attraction than in the other. Stereo-isomers of this kind show greater differences both chemically and physically than the compounds whose stereo-chemical isomerism has been treated of under (1) and (2) (see p. 22). The one isomer, in contradistinction to the other, is often characterized by a definite intra-molecular reaction, *e.g.* the formation of an anhydride, this being induced by the spacial approximation of the reacting atoms or atomic groups towards one another, in consequence of the configuration.

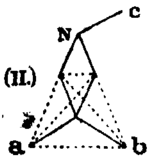
The interesting isomerism of fumaric and maleic acids—to give an instance—has been clearly explained by the above theory, the value of which has been enhanced by the fact that this explanation has led to the discovery of other cases of isomerism in unsaturated compounds (chloro-propylene, chloro-crotonic acid, etc.).

4. A nitrogen atom may also give rise to isomerism in this way, if its three affinities do not act in one and the same plane, but in a similar direction, as from one corner of a tetrahedron to the three others. Thus, of the compound—

$$\begin{matrix} a \\ b \end{matrix}\!>\!C=N—c,$$

the two following modes of spacial arrangement of the atoms are conceivable (the affinity-directions are here represented by straight lines, and the edges of the carbon-atom tetrahedra by dotted ones):—





or, abbreviated:—

a—C—*b*
  ||
 N—*c*

and

a—C—*b*
  ||
 c—N

What has just been said under (3) applies here also, viz. that it is easy to conceive that the groups or atoms, *a* and *c*, would exert a stronger mutual influence in the one case than in the other, and would thus give rise to outward differences in the two substances represented by the above formulae.

This conception is of especial value for the explanation of the observed cases of isomerism among the ketoximes (which see).

Cf. *Hantzsch* and *Werner*, B. **23**, 1; **24**, 3511; **25**, 2164; *V. Meyer*, B. **23**, 567.

5. While the nitrogen-isomerism, which has just been described, corresponds in many respects with the carbon-isomerism treated of under paragraph (3), a nitrogen-isomerism among compounds *containing pentavalent nitrogen* [cf. nitrogen bases, behaviour of, paragraph (7)] has been met with, which resembles the carbon-isomerism spoken of under paragraph (1). (*Le Bel*, B. **24**, Ref. 441.)

6. The above cases of isomerism must not be confounded with dimorphism, which exists among many inorganic, as well as among certain organic, compounds.

On the other hand, there are also numerous cases known in which two different constitutional formulae may be ascribed with equal correctness to one and the same substance, according to its behaviour in different reactions. Such formulae are termed *tautomeric.*—For further particulars see the Cyanogen Compounds, Section F.

Rational Formulae.

Great latitude is permissible as regards the mode of writing constitutional formulae, according to the particular points which it is desired to emphasize. A formula on paper is not as a rule intended to represent the symmetrical or other arrangement of the atoms in a compound.

A shortened constitutional formula, which indicates more chemical relations than an empirical one does, is called a *rational* formula; *e.g.* C_2H_5OH, alcohol; $(CH_3)_2O$, methyl ether.

For acetic acid, instead of the constitutional formula already given on page 19, the following rational formulae may be used—

$$CH_3{-}C{\lessdot}^{O}_{OH},\quad CH_3{-}CO.OH,\quad CH_3{-}CO_2H,\quad CH_3.CO_2H,$$
$$(CH_3.CO)OH,\quad C_2H_3O.OH,\quad H(C_2H_3O_2),\ \text{and so on.}$$

Homology.

On replacing the hydrogen in methane by 1, 2, 3, or 4 atoms of chlorine, the substitution products, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 result. The halogen in these can, in its turn, be replaced by oxygen (Cl by OH, 2Cl by O, and 3Cl by O and OH together); in this way we obtain the following compounds—

CH_3OH.	CH_2O.	$CHO.OH$ or CH_2O_2.
Methyl alcohol.	Formic aldehyde.	Formic acid.

From ethane, C_2H_6, which so closely resembles methane, similar compounds are derivable, compounds which, in their chemical properties, are in every respect analogous to those from methane, but differ from them in composition by the addition of CH_2.

The same holds good for compounds with three and more carbon atoms. Thus, corresponding to methane and ethane, we have propane, C_3H_8, butane, C_4H_{10}, etc.; to methyl alcohol and ethyl alcohol, propyl alcohol, $C_3H_7.OH$, and so on.

Substances which differ from each other in composition by a constant quantity such as CH_2 or some multiple of CH_2, and which at the same time resemble each other closely in their chemical behaviour, are termed homologous, and can be arranged in "homologous series," thus—

CH_4 Methane.	CH_3Cl Methyl chloride.	$CH_3.OH$ Methyl alcohol.	CH_2O Formic aldehyde.	CH_2O_2 Formic acid.
C_2H_6 Ethane.	C_2H_5Cl Ethyl chloride.	$C_2H_5.OH$ Ethyl alcohol.	C_2H_4O Acetic aldehyde.	$C_2H_4O_2$ Acetic acid.

C_3H_8 Propane.	C_3H_7Cl Propyl chloride.	$C_3H_7.OH$ Propyl alcohol.	C_3H_6O Propionic aldehyde.	$C_3H_6O_2$ Propionic acid.
C_4H_{10} Butane.	C_4H_9Cl Butyl chloride.	$C_4H_9.OH$ Butyl alcohol.	C_4H_8O Butyric aldehyde.	$C_4H_8O_2$ Butyric acid.

The following general formulae can also be given for these series—

C_nH_{2n+2}. | $C_nH_{2n+1}Cl$. | $C_nH_{2n+1}.OH$. | $C_nH_{2n}O$. | $C_nH_{2n}O_2$.

A new *International Nomenclature* (1892) is based upon the same principle of the derivation of all organic compounds from the hydrocarbons containing an equal number of carbon atoms with themselves. The *official names* of all compounds are formed by attaching certain suffixes to the unaltered names of the hydrocarbons. The addition of the syllable "*ol*" indicates a hydroxyl, of the syllable "*al*" an aldehyde, and of the word "*acid*" a carboxyl group, and so on. For instance, the derivatives of butane mentioned in the above table are named Butane, Chloro-butane, Butanol, Butanal, and Butanoic acid. The presence of 2, 3, or more substituents is shown by the interpolation of the syllables *di*, *tri*, etc., while the insertion of numerals gives the positions of these substituents (an end-carbon atom being marked "1"). The official names of the acids of the methane series are derived from those of the hydrocarbons containing an equal number of carbon atoms in the molecule, *e.g.* *Butane di-acid* for succinic acid (instead of ethane-dicarboxylic acid). For further details, see *F. Tiemann*, B. **26**, 1595; Rec. Tr. Ch. **11**, 1; *Nature* (1892), 56–59; and also the special part of this book, where, in dealing with the more important classes of compounds, mention is made of the international nomenclature, if it deviates from the system already in use, and where the official name ("O.N.") of individual compound is frequently added in brackets.

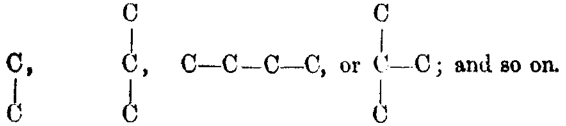
Homology constitutes a most important aid in the study of organic chemistry, because the compounds belonging to a homologous series nearly always show analogous properties, and thus the study of a single member often suffices for the whole group.

From a physical point of view, it is observable that, with an increase in the number of carbon atoms, the tendency of the compounds is to change gradually from the gaseous to the liquid or solid state. Thus, the compound C_3H_8 is gaseous, C_5H_{12} is liquid at the ordinary temperature, $C_{10}H_{22}$ also liquid, but with a rather high boiling point (173°), while $C_{20}H_{42}$ is solid, boiling only above 300°. Similarly, formic acid is liquid, and the corresponding acid with 16 atoms of carbon solid; the former boils at 99°, the latter at over 300°.

But more lies in homology. All the homologues of methane, CH_4, contain the maximum number of hydrogen atoms which can be taken up by the number of carbon atoms in question, viz., $2n+2$ atoms of hydrogen for n atoms of carbon; under no circumstances can more hydrogen than this be bound.

Just as ethane can be derived from methane by substituting for H the monovalent group CH_3, the composition-difference CH_2 following as a consequence of the tetravalence of carbon, so are all the higher hydrocarbons of this series derived from those poorer in carbon by the continuous exchange of H for CH_3; thus the formula of all the higher homologues is $CH_4 + (n+1).CH_2$, *i.e.* C_nH_{2n+2}. The tetravalence of carbon is therefore manifestly the cause of the homology.

The grouping together of the carbon atoms must thus be conditioned by themselves, since hydrogen, as a monovalent *element, cannot be the cause of it.* In all the higher hydrocarbons, the carbon atoms are therefore combined together in the form of a chain, as it were, as the following graphical representation shows:



in C_2H_6. in C_3H_8. in C_4H_{10}.

Various cases can occur in the mode of combination of the carbon atoms (Isomers). (See Hydrocarbons of the Methane Series.)

Law of Even Numbers of Atoms.

The number of hydrogen atoms in the above hydrocarbons is always divisible by two. Should they therefore be partially replaced by other elements, the sum of these latter, if their valencies are expressed by odd numbers, *e.g.* Cl, N, and P, and of the remaining hydrogen atoms taken together must, as a necessary consequence of the law of equivalent proportions, remain an even number.

Radicles.

According to *Liebig*, radicles were groups of atoms capable of a separate existence, which played the parts of elements, and, like these latter, could combine among themselves and be exchanged from one compound to another.

Later on, the postulate that such radicles must also be capable of existing in the free state was allowed to lapse, and they were frequently defined shortly as "the residues left unattacked by certain decompositions."

Now, however, it is usual to designate as radicles only those atomic groups which are found repeating themselves in a comparatively large number of compounds derived from one another,

and which play in these compounds the part of a simple element, *e.g.* CH_3, methyl, C_2H_3O, acetyl; by this definition the question of their capability of existence when isolated does not come up. The radicle methyl, for example, is not known in the free state, since, when its formation might be expected, ethane (di-methyl), $CH_3—CH_3$, is obtained instead (see p. 17). Such radicles may be mono-, di-, or tri-valent, etc., according to the number of monovalent atoms which they are capable either of replacing or of combining with, so as to form a saturated compound; for instance, $(C_2H_4)''$, ethylene, is divalent; $(C_3H_5)'''$, glyceryl, trivalent; $(CH)'''$, methine or methenyl, likewise trivalent, etc. The monovalent residues, C_nH_{2n+1} (methyl, ethyl, etc.), which form the radicles of the monovalent alcohols, $C_nH_{2n}OH$, are frequently termed *alkyls*, while the divalent residues, C_nH_{2n}, are known as *alkylenes*.

Classification of the Hydrocarbons, etc.

The hydrocarbons which have already been described are termed "saturated" compounds, since they cannot take up more hydrogen. But besides these there are hydrocarbons, etc., poorer in hydrogen, or "unsaturated," such as C_2H_4, ethylene, and C_2H_2, acetylene, corresponding to which there are likewise homologous series.

The constitution of these is explained, as will be seen later, by the assumption of a double or triple bond between neighbouring carbon atoms, for instance—

$$C_2H_4 = \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}; \qquad C_2H_2 = \begin{array}{c} CH \\ ||| \\ CH \end{array}.$$

From these different hydrocarbons, as starting points, the most various substitution products, such as alcohols, aldehydes, ketones, acids, etc. (see p. 27), are derived by exchange of the hydrogen for halogen, oxygen, nitrogen, etc.

To another class of hydrocarbons belongs that most important compound benzene, C_6H_6, which contains eight atoms of hydrogen less than hexane, C_6H_{14}. With regard to its constitution, the theory of the existence of a closed chain of six carbon atoms has been advanced. (See Benzene Derivatives.) From benzene are derived an immense number of the most different homologous and analogous hydrocarbons and substitution products, alcohols, aldehydes, acids, and so on.

Thus benzene, like methane, is the mother substance of numerous organic compounds.

What has just been said with regard to benzene also holds good for various other compounds, which are characterized from a chemical point of view by containing a closed (ring) chain. These are:—

(*a*) Trimethylene, C_3H_6; Tetramethylene, C_4H_8; and Pentamethylene, C_5H_{10}.

(*b*) Pyridine, C_5H_5N, a strongly basic nitrogenous compound, but one which at the same time resembles benzene closely in many respects.

(*c*) Furfurane, C_4H_4O; Pyrrol, C_4H_5N; Thiophene, C_4H_4S; Pyrazole, $C_3H_4N_2$; Thiazole, C_3H_3NS; etc.

Some of these latter compounds are extremely like benzene, others like pyridine; several of them are as yet only known in the form of derivatives. Like benzene, they are all mother-substances for—in many cases—long series of compounds.

Organic chemistry is therefore divided into the two following sections:—

1. Chemistry of the Methane Derivatives or Fatty Compounds, or Aliphatic Compounds (from ἀλοιφή, fat), so called because the fats and many of their derivatives belong to this group. This section comprises all carbon compounds with open chains.

2. Chemistry of the Benzene Derivatives or Aromatic Compounds. While retaining this classification, the compounds mentioned above under *a* and *c* will be treated of at the end of Section I., because they constitute to some extent a bridge between the fatty and the aromatic series; on the other hand, for convenience' sake, pyridine and its derivatives will not be considered until after those of benzene have been discussed.

Physical Properties of Organic Compounds.

The physical properties of organic compounds are often of the greatest importance for their characterization. They frequently show a more or less regular relation to the composition and constitution of the compounds. A few of these may be mentioned here.

Colour.

Most organic compounds are colourless; compounds containing iodine and nitro-compounds are frequently yellow or red.

Many substances are converted into dyes, or their leuco-compounds, by the entrance of the salt-forming groups NH_2 or OH; for instance, triphenyl-carbinol and azo-benzene (see these); those substances are termed "chromogenes." (*Witt*, B. **9**, 522).

Solubility.

The hydrocarbons and their substitution products are either insoluble, or only slightly soluble in water. While the lower members of a homologous series of the alcohols, such as methyl and ethyl alcohols and glycerine, dissolve for the most part easily in water, the higher homologues are either difficultly soluble or insoluble. The polyatomic (polyhydric) alcohols, *e.g.* mannite, are readily soluble in water, but unlike the monatomic, are mostly insoluble in ether. Aldehydes, ketones, and acids behave similarly to alcohols. The benzene derivatives are, as a rule, less soluble in water and alcohol than the analogous fatty compounds.

Most organic compounds dissolve in alcohol, and the greater proportion in ether.

Specific Gravity and Molecular Volume.

The specific gravities of isomeric compounds are different. Those of the normal hydrocarbons, determined at their melting points, approach—with increase of carbon—to a definite limit (about 0·78), which is already almost reached in the case of $C_{16}H_{34}$. (See the Paraffins.)

The specific gravities of the normal hydrocarbons, C_nH_{2n} and C_nH_{2n-2}, from C_{12} onwards, likewise approach this limit, but more slowly and in a downward direction; thus, $C_{18}H_{36}$ has the specific gravity 0·791, and $C_{18}H_{34}$ that of 0·802. The specific gravities of the monobasic fatty acids, beginning at a number greater than 1, also sink with increasing carbon and approach to the above-mentioned limit, only very much more slowly than in the case of the hydrocarbons.

The Molecular Volume, sometimes also termed the Specific Volume, is the quotient from the molecular weight and the specific gravity.

By comparing the molecular volumes of liquids under similar conditions, *i.e.* at their boiling temperatures, *H. Kopp* a long time ago, and with the material then available, observed certain approximate relations, which allowed of expression in these words: the molecular volume of a compound is equal to the sum of the atomic volumes of its constituent elements.

(A. **46**, 212; **92**, 1; **94**, 269; **96**, 171, etc.) Thus, in homologous series an increase of about 22 was observed for each CH_2, and in this way it appeared possible to deduce from the molecular volume of compounds the atomic volumes of their constituent elements. For carbon this was found to be 11, and for hydrogen 5·5. For the polyvalent elements, especially for oxygen and nitrogen, varying values were obtained by calculation, the value appearing to depend upon the mode in which the elements were combined. Thus, the O which was joined to C by a double bond in a compound had the volume 7·8, while that joined by a single one had the volume 12·2.

Later investigations, which have had much more material to work upon in consequence of recent discoveries, have shown that the above law is only approximately true. Thus isomeric bodies have not the same, but somewhat different molecular volumes. In unsaturated compounds each double bond of C to C appears to increase the molecular volume. Compounds which contain the carbon atoms combined in the form of a ring (p. 20), have a distinctly smaller molecular volume than the isomeric compounds with an open chain and with two carbon atoms linked together by a double bond (*Horstmann*, B. **20**, 766). Even when their atoms are similarly linked, isomeric bodies have different molecular volumes: for example, ethylene chloride and ethylidene chloride, whose molecular volumes differ by 4 per cent of their value.

It follows from this that the molecular volumes of organic compounds are apparently conditioned by two influences: the one is of an "additive" nature—the atomic volumes add themselves together according to the laws worked out by *Kopp;* the other is of a "constitutive" nature: the mode in which the various constituent elements are linked chemically produces differences in the volume.

(Cf. *Thorpe*, Ch. Soc. J. **37**, 141; *Lossen* and his Pupils, A. **211**, **214**, **221**, **233** and **254**; *Schiff*, A. **220**, 71; *Staedel*, B. **15**, 2559; *Horstmann*, B. **19**, 1579; *Kopp*, A. **250**, 1, and others.)

Laws regulating the Boiling Point.

1. In homologous compounds the boiling point rises, in the case of substances of analogous constitution, by an increment for each CH_2 which is constant in the lower members of the series; this is 19°–20° for each CH_2 in the lower members of the methyl alcohol and formic acid series, and 30° in the series of the methylated benzenes (containing the methyl group in the benzene ring). In the higher members of a series, *i.e.* with increasing carbon, the temperature-difference decreases. (See, as an example, the Methane Series.)

2. The boiling points of the normal hydrocarbons of the series C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-2} are very near to each other; *e.g.* $C_{16}H_{34}$, 181·5°, $C_{16}H_{32}$, 179°, and $C_{16}H_{30}$, 184°.

3. In the case of isomeric substances, the normal compound in the fatty series has the highest boiling point; the more branching the C-chain is, the lower is the boiling point. (See the Hydrocarbons C_5H_{12} and the Acids $C_5H_{10}O_2$.)

4. The entrance of halogens generally raises the boiling point considerably, the first Cl-atom, for instance, by about 60°, and the succeeding ones by a less amount. (See, *e.g.*, Chlorinated Methanes and Acetic Acids.)

5. On comparing compounds which contain hydroxyl with the substances from which they are derived, it is seen that the entrance of the OH group has caused a considerable rise in the boiling point; and, further, that while the mother substance may distil unchanged, the hydroxyl derivative frequently decomposes upon distillation. Thus, propionic acid is volatile, while lactic acid (oxy-propionic) is not.

6. The boiling points of ethers (see these) are considerably lower than those of the isomeric alcohols, or even of the corresponding alcohols; thus, ethyl ether boils at 35°, the isomeric butyl alcohol at 117°, and ethyl alcohol at 78°. The same thing applies to the compounds derived from the alcohols by exchange of OH for SH or NH_2 (mercaptan, C_2H_5SH, boils at 36°; ethylamine, $C_2H_5NH_2$, at 18°); and to the glycols and their simple ethers (glycol boils at 197°, ethylene oxide at 13°).

7. Aromatic ortho- di-derivatives are more easily volatilized than the isomeric para-derivatives, etc., etc.

8. Many substances which decompose on distillation under the ordinary atmospheric pressure, can be volatilized unchanged in a vacuum, the boiling points being thus reduced by 100° or more. For the relations between boiling point and (diminution of) pressure, see, *e.g.* B. **23**, 1254; **24**, 736; also *Thorpe's* Dict. of Applied Chemistry, **1**, 690.

Fractional Distillation.

The separation by distillation of two substances which boil at different temperatures can only be carried out easily when the interval between the boiling points is a large one. If these only differ from one another slightly, say by 10°–30°, the tension of the vapour of the higher boiling liquid is already so considerable at the temperature at which the lower one boils, that it partly distils over with the latter. As a consequence, one observes in such cases a continuous rise of the thermometer without its remaining stationary at any given boiling point, and a gradual (not intermittent) change in the composition of the distillate.

In such cases one must distil "fractionally," *i.e.* the distillate must be collected in separate "fractions," according to the rise of boiling point, *e.g.* from 5° to 5°, and each of these fractions must be again fractionated by itself. The operation has to be repeated until the middle fractions have been separated into the higher and lower boiling constituents, *i.e.* until the separation of these latter has been effected. To facilitate the operation, apparatus is used which favours a partial condensation of the vapour, by which means the vapour of the higher boiling substance is mostly liquefied; (fractionating apparatus by *Wurtz*, *Linnemann*, *Glinsky*, *Henninger*, *Le Bel*, *Hempel*, *Warren*). On the large scale, apparatus depending upon the same principle and called "column apparatus" and "dephlegmators," are employed for separating the benzene hydrocarbons and for purifying alcohol.

Even with liquids whose boiling points are relatively wide apart from one another, cases may arise in which a separation by fractional distillation is difficult or even impossible. As an example of the latter, it may be mentioned that a mixture of 2 volumes water with 3 volumes amyl alcohol (B. Pt. 135°) boils at the constant temperature of 96°, and a similar mixture of carbon bisulphide and water at 43°.

When two substances which do not mix with one another, or whose vapour tensions are not altered upon mixing, are distilled together, the quantity of each which passes over is proportional to the product of the vapour tension at the boiling temperature of the mixture into the vapour density. (G : g = MP : mp, where m. is the molecular weight, g. the weight in the distillate, and p. the vapour tension of the one constituent at the boiling temperature of the mixture, M.G.P. being the corresponding values for the other constituent. *Wanklyn's* law, corroborated by *Berthelot* and *Thorpe*.) Since, in gases and vapours, the molecular weight is proportional to the specific gravity, it is possible to calculate by this law the molecular weight of a substance from the observed proportions in which two constituents of a mixture distil, provided the molecular weight of the other, *e.g.* water, is known (*Naumann*).

*Laws Regulating the Melting Point.**

1. One frequently observes in homologous series that the melting points of the successive members alternately rise and fall in such a manner that the members with an odd number of carbon atoms have a

* For laws regulating the melting point of organic compounds, see, *e.g.* B. 23, 2389.

lower melting point than those containing an atom of carbon less, while the melting points of the members, both with odd and with even numbers of carbon atoms, when regarded alone, rise regularly (formic acid series), or also in part fall (succinic acid series).

2. Of the isomeric di-derivatives of benzene, the *p*-compounds have the highest melting point, and are often solid when the *m*- and *o*-compounds are still liquid. The lengthening out of the side chains causes a lowering of the melting point.

3. In compound ethers, the methyl ethers have frequently a higher melting point than the ethyl, and the ethyl a higher one than the propyl, etc.; thus the methyl ether of oxalic acid is solid, and the ethyl ether liquid.

4. The melting point of a mixture of two substances alters with its composition in this way, that, with a definite composition, a minimum of melting point is attained, which lies below that of the lower melting constituent. As examples of this may be mentioned a mixture of stearic and palmitic acids, which, on account of its lower melting point, was for long held to be a separate acid, "margaric acid"; or a mixture in equal proportions of para- and meta-oxybenzoic acids, which melts at 143°–152°, while the acids separately melt respectively at 210° and 290°.

Even very small quantities of admixtures may materially reduce the melting point of a compound. The constancy of the melting point of a substance after repeated recrystallizations is therefore a valuable criterion of its purity.

Electrical Behaviour.

According to Ostwald, the electrical conductivity of organic and also of inorganic acids, in solutions of gradually decreasing concentration, affords a means of determining the strength, *i.e.* power of affinity, of these. For details see *Ostwald's* "Grundriss der Allgemeinen Chemie" (Leipzig, 1889); or *Walker's* translation of *Ostwald's* "Outlines of General Chemistry" (Macmillan & Co., 1890).

Heat of Neutralization.

The value of the heat of neutralization of organic acids in aqueous solution by caustic soda is approximately the same for the organic carboxylic acids, *i.e.* for those which contain the radicle

carboxyl, COOH, in so far as their salts are not decomposed by water, being as a rule somewhat over 12,000 calorimetric units. Phenols give only about half this value, while for ordinary alcohols under similar conditions it is very small. Use can be made of this to determine the function of the hydroxyl in any compound. The entrance of a negative radicle, such as NO_2, into a phenol, which converts it into an actual acid, is also accompanied by a rise in the heat of neutralization (*Berthelot*).

Heat of Combustion and Heat of Formation.

Certain relations are likewise observable on comparing the heats of combustion of different substances, molecule for molecule. Thus the molecular heat of combustion increases in most homologous series by 150,000 to 160,000 calorimetric units for each atom of carbon.

In isomeric compounds the heats of combustion are equal when the chemical nature of the compounds is the same, *e.g.* in the case of methyl acetate and ethyl formate, but different when the constitution is different; thus the heat of combustion of allyl alcohol is greater than that of acetone, and that of di-propargyl materially higher than that of benzene. (*Cf.*, *e.g.*, B. **24**, 650.)

From the heat of combustion the heat of formation of a substance, which appears to be very closely connected with its constitution (although the laws which regulate this have not yet been clearly elucidated), can be calculated. For particulars of these interesting relations, *Thomsen's* "Thermochemische Untersuchungen," vol. 4, and *Brühl*, J. pr. Ch. **35**, 181, 209, must be consulted.

Optical Behaviour.

1. *Refractive Power.*

The formula $\frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{M}{\rho}$ expresses the Molecular Refraction of a liquid (μ representing the index of refraction, M the molecular weight, and ρ the density), which is almost independent of the temperature. This value alters almost equally with equal differences in composition. It is nearly the same in the case of compounds which are position-isomers, *e.g.* propyl and isopropyl alcohols, but is dissimilar in the case of saturation-isomers, such as acetone and allyl alcohol. The molecular refraction of a compound is approximately equal to the sum of the atomic refractions of its constituent elements. The atomic refractions of the monovalent elements are constant, but those of the polyvalent elements, carbon or oxygen for instance, vary

with the mode in which the atoms are joined together, being increased by almost constant increments through the so-called double or treble linking (which see). It is thus possible to deduce the constitution of a compound from its observed molecular refraction. For instance, we can say by this means with tolerable certainty whether, in an unsaturated compound C_xH_{2y}, the carbon atoms are doubly linked, or linked together in the form of a ring, and also how many of each of those linkings there may be. (Cf. *Brühl*, A. **200**, 139; **203**, 1, 255, 363; **211**, 121, 371; **235**, 1; Z. phys. Chem. **1**, 307; **7**, 1, 140; B. **24**, 1815.)

2. *Behaviour towards Polarized Light (Circular Polarization).*

Cf. *Landolt's* "Das Optische Drehungsvermögen organischer Substanzen" (Vieweg).

Many organic compounds turn the plane of polarization of light,—they are "optically active." Some only effect this when in the crystalline state, and not when amorphous or fused, thus showing that the property depends upon their crystalline structure, *e.g.* benzile, $C_{14}H_{10}O_2$; one (sulphate of strychnine) both when crystalline and amorphous; most of them, however, only when in the amorphous liquid condition or dissolved, *e.g.* tartaric acid, cane sugar, etc. Oil of turpentine and camphor also possess this property when in the state of gas, and it must therefore in their case be dependent upon the arrangement of the atoms and not of the molecules.

The turning of the plane of polarization is proportional (1) to the thickness of the layer of the solution l to be traversed, and (2) to the percentage of compound p in it. If the observed angle of deflection α be reduced to the length of 1 decimetre of the layer traversed, and to 1 gramme of the active substance in 1 cubic centimetre of solution ($\alpha = p\rho/100$, where ρ = the specific gravity of the solution), then the "specific rotatory power" of the substance is:

$$[\alpha] = \frac{100\alpha}{lp\rho}.$$

This specific rotatory power to right (+), or to left (−), is constant and characteristic for each substance dissolved in a given solvent, and of a given concentration and temperature. It diminishes as a rule with rise of temperature, and increases with increasing dilution, and it is also dependent upon the nature of the solvent and of any possible admixture.

Thus asparagine and aspartic acid in alkaline solution turn the plane to the left, in acid solution to the right. Dextro-tartaric acid, with increasing concentration of the solution, turns it less and less to the right; when it contains 100 per cent., *i.e.* when fused, it turns it to the left.

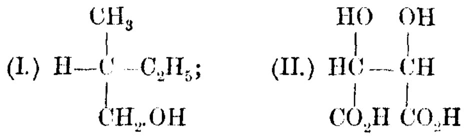
By eliminating the (calculated) influence of the solvent, we obtain the "real specific rotation" (*Landolt*). This is usually given for yellow sodium light, *i.e.* *Fraunhofer's* D-line, and designated as $[\alpha]_D$.

These optical relations are sometimes complicated by the presence of the so-called "multi-rotation." (See grape and milk sugars.)

It has now been proved in many cases that several optically different modifications of the same compound exist; there are, for instance, a dextro-rotatory and an equally strong laevo-rotatory tartaric acid, by the combination of which an inactive tartaric acid (racemic acid) is formed (*Pasteur*, 1848). The last-named can be broken up into the two active modifications, in contradistinction to another inactive tartaric acid which is not thus divisible. Malic acid likewise exists in several optically different modifications. In the case of various other compounds, only one such modification has as yet been observed. Optically inactive modifications, which result like racemic acid from the conjunction of two active components, are termed "racemic" modifications. When the active compounds which occur in nature are prepared artificially in the laboratory, they are almost always inactive, the racemic modifications being obtained (for exceptions to this rule, see, for instance, A. **270**, 69). A transformation or splitting up of these latter into the optically active modifications can sometimes be effected in the case of acids by the crystallization of their salts, *e.g.* the cinchonine salts and the double Na-NH_4-racemate, and also by the addition of certain ferments, in especial the *Penicillium glaucum* and the *Schizomycetes*. The action of the latter is explained by their assimilating the one active modification more rapidly than the other. In certain cases both of the active components crystallize out separately from aqueous solutions of racemic modifications (B. **25**, 1026).

The optically active modifications, which may also show slight differences from a chemical point of view, can usually be transformed one into the other, — and also partially into the inactive forms, — by warming with water, or with quinoline or pyridine, to 140°–170°.

According to *Le Bel* and *van 't Hoff*, the optical activity is determined by the presence of one or more *asymmetric* carbon atoms, *i.e.* carbon atoms which are joined by their four affinities to four different elements or groups, as, for instance, in active amyl alcohol (I.), and in tartaric acid (II.):



The point has already been discussed (on p. 23) as to how the presence of asymmetric carbon atoms explains the existence of such optically different modifications. Supposing that in the tetrahedra, drawn upon p. 23, the corners marked *A* are occupied by atoms of hydrogen, while those marked *B*, *C*, and *D* are occupied respectively by the groups CH_3, C_2H_5 and OH; then it is easy to see that if dextro-rotation is caused by those groups following one another in the direction of motion of the hands of a watch, the opposite order of succession must give rise to an equally strong laevo-rotation.

As a matter of fact, all optically active substances contain asymmetric carbon or nitrogen atoms. (B. **24**, Ref. 441.)

On the other hand, every compound which contains an asymmetric carbon atom is not necessarily optically active, (1) because inactivity may be induced by the nature of the groups B, C and D, and (2) because it will usually happen that a compound, whose molecules are individually active, will contain dextro- and laevo-rotatory molecules in equal numbers, and thus their separate actions will be neutralized. (For an explanation of the optical activity see also B. **24**, 101.)

For further details, see under tartaric acid.

SPECIAL PART.

Class I.—METHANE DERIVATIVES.

I. HYDROCARBONS.

A. Saturated Hydrocarbons, C_nH_{2n+2}.

Summary.

		M.Pt.	B.Pt
CH_4	Methane,	-186°	-164°
C_2H_6	Ethane.		Gas.
C_3H_8	Propane,		-17°
	BUTANES.		
C_4H_{10}	(1) Normal-butane,		+1°
C_4H_{10}	(2) Iso-butane,		-17°
	PENTANES.		
C_5H_{12}	(1) Normal-pentane,		+28°
C_5H_{12}	(2) Iso-pentane,		+30°
C_5H_{12}	(3) Tertiary-pentane,	-20°	+9°
C_6H_{14}	Hexane,		71°*
C_7H_{16}	Heptane,		98°
C_8H_{18}	Octane,		124°
C_9H_{20}	Nonane,	-51°	150°
$C_{10}H_{22}$	Decane,	-32°	173°
$C_{11}H_{24}$	Undecane,	-26°	195°
$C_{12}H_{26}$	Dodecane,	-12°	214°

		M.Pt.	B.Pt.
$C_{13}H_{28}$	Tridecane,	-6°	234°
$C_{14}H_{30}$	Tetradecane,	+5°	253°
$C_{15}H_{32}$	Pentadecane,	+10°	271°
$C_{16}H_{34}$	Hexadecane,	18°	288°
$C_{17}H_{36}$	Heptadecane,	23°	303°
$C_{18}H_{38}$	Octadecane,	28°	317°
$C_{19}H_{40}$	Nonadecane,	32°	330°
$C_{20}H_{42}$	Eicosane,	37°	{205°†
$C_{21}H_{44}$	Heneicosane,	40°	{215°
$C_{22}H_{46}$	Docosane,	44°	{225°
$C_{23}H_{48}$	Tricosane,	48°	{234°
$C_{24}H_{50}$	Tetracosane,	51°	{243°
—	—	—	—
$C_{27}H_{56}$	Heptacosane,	60°	{270°
—	—	—	—
$C_{31}H_{64}$	Hentriacontane,	68°	{302°
$C_{32}H_{66}$	Dicetyl,	70°	{310°
—	—	—	—
$C_{35}H_{72}$	Penta-triacontane,	75°	{331°
$C_{60}H_{122}$	Hexacontane,	101°	—

* All the numbers given from hexane onwards refer to the normal hydrocarbons. (See below.)

† { signifies boiling point under 15 mm. pressure.

The first members of the series up to those with about four atoms of carbon are gases, which gradually become more easily condensable as the number of carbon atoms in the molecule increases. The members which follow are liquid at the ordinary temperature, their boiling point rising with increasing number of carbon atoms. The higher homologues, from about $C_{16}H_{34}$ (melting point 18°) on, are solid at the ordinary temperature. They boil finally without decomposition only under diminished pressure and at very high temperatures, while their melting point gradually rises up to about 100°. The methane homologues are almost or quite insoluble in water; alcohol dissolves the gaseous members to a slight extent, the liquid members easily, and the solid with gradually increasing difficulty. Their specific gravities at the melting point increase with increasing number of carbon atoms from 0·4 up to 0·78, which forms a boundary limit. This value is already almost reached by the hydrocarbon $C_{11}H_{24}$, so that for the higher members of the series the following law holds good: "the molecular volumes are proportional to the molecular weights" (*Krafft*).

They are incapable of combining further with hydrogen or halogens (see p. 28), and absorb neither bromine nor sulphuric acid. They are therefore termed the Saturated Hydrocarbons. Even fuming nitric acid has little or no action upon them; thus, methane is not attacked by a mixture of fuming nitric and sulphuric acids, even at 150°. They are also very indifferent towards chromic acid and permanganate of potash in the cold; when oxidation does take place, they are mostly converted directly into carbonic acid. The name of "The Paraffins," (from *parum affinis*), which was originally applied only to the solid hydrocarbons from lignite, has therefore been extended to the whole homologous series.

By the action of the halogens, (Cl, Br), substitution takes place, the substituted hydrogen combining with an amount of halogen equal to that which has entered the hydrocarbon, (see Substitution products of the Hydrocarbons):

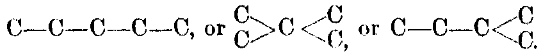
$$CH_3H + ClCl = CH_3Cl + HCl,$$

The percentage composition of these hydrocarbons approaches with increasing carbon to a definite limit, viz. to that of the hydrocarbons, $C_nH_{2n} = CH_2$, as is shown by the following table :

Per cent.	CH_4	C_2H_6	C_3H_8	C_6H_{14}	$C_{16}H_{34}$	$C_{22}H_{46}$	$C_{24}H_{50}$	$C_{35}H_{72}$	Limit Value, C_nH_{2n}
C	75·00	80·00	81·82	83·72	84·60	85·16	85·21	85·36	85·71
H	25·00	20·00	18·18	16·28	15·40	14·84	14·79	14·64	14·29

It is therefore impossible to distinguish by elementary analysis between two of the neighbouring higher homologues, *e.g.* C_{22} and C_{24}, C_{24} and C_{30} ; the only reliable data here are the methods of formation from compounds in which the number of carbon atoms in the molecule is already known, and the melting points.

Isomers.—Only one representative each of the formulae CH_4, C_2H_6, and C_3H_8 is known, but of C_4H_{10} there are two, of C_5H_{12} three, and of C_6H_{14} already five isomers, and most of the higher hydrocarbons are known in various isomeric forms. From this the conclusion is drawn that in these different isomers the carbon atoms are differently combined, in the one case, as it were, in a straight line without branching, like the links of a chain ; in the other, with the formation of a branching chain. (This is of course not to be taken as meaning that they are grouped together in space in straight lines.) Thus :



The first of these hydrocarbons, with a non-branching chain, are termed the normal hydrocarbons ; the last, the iso-hydrocarbons. (See p. 49.)

The principles by which such constitutional formulae are arrived at will be explained under Butane and Pentane.

Only those homologues are comparable whose constitutions are similar, as in the case of the normal hydrocarbons.

Occurrence.—The hydrocarbons of the paraffin series occur naturally in great variety. Thus, methane is exhaled from

the earth's crust, as pit gas and as marsh gas. The next higher homologues are found dissolved in petroleum, which also contains the higher hydrocarbons in large amount. Solid hydrocarbons occur as ozokerite or earth wax. By the fractional distillation of petroleum, a large number of these compounds have been isolated. Heptane and hexadecane are also found in the vegetable kingdom.

Modes of formation.—A. The gaseous as well as the liquid and solid members of this series are obtained by the distillation of lignite (Boghead-, Cannel coal), wood, bituminous shale, and, in very much smaller quantity, from pit coal. Paraffins are also got by dissolving carbide of iron in acids, and by heating wood, lignite, and coal, but not graphite, with hydriodic acid.

A mixture of paraffins, very similar to petroleum in its composition, results from the decomposition of fats (train-oil) by heat under a high pressure (*C. Engler*, B. **21**, 1816).

B. From substances containing an equal number of carbon atoms in the molecule.

1. From the halogen alkyls,* $C_nH_{2n+1}X$, and, generally speaking, from the substitution products of the hydrocarbons by exchange of the halogen for hydrogen (backward substitution). This is effected by the action of sodium amalgam, or of zinc and hydrochloric acid, by heating with water and zinc to 160° (*Frankland*), or with fuming hydriodic acid, which last is a most energetic reducing agent, especially in the presence of red phosphorus; and so on.

Heating with anhydrous chloride of aluminium has a similar effect.

$$C_2H_5I + HH = C_2H_6 + HI.$$

$$CH_3I + HOH + Zn = CH_4 + \underbrace{Zn\begin{cases}OH\\I.\end{cases}}_{\text{Basic iodide of zinc.}}$$

$$C_2H_5I + HI = C_2H_6 + I_2.$$

2. From the monatomic alcohols, $C_nH_{2n+1}OH$.

a. By first converting them into the corresponding halogen compounds, *e.g.* by means of halogen hydride, and then transforming those, according to 1, into the paraffins.

Krafft has prepared the higher normal paraffins from these

* The monovalent residues, C_nH_{2n+1}, methyl, ethyl, etc., which are at the same time the radicles of the monatomic alcohols, $C_nH_{2n+1}OH$, are frequently termed alkyls.

halogen-alkyl compounds, by splitting off the halogen hydride and heating the residual C_nH_{2n} with HI. (B. 16, 1714.)

b. By heating directly with hydriodic acid—

$$C_2H_5OH + 2HI = C_2H_5I + H_2O + HI = C_2H_6 + H_2O + I_2.$$

Also by heating polyatomic alcohols, such as glycerine, with hydriodic acid to a high temperature.

3. From compounds richer in oxygen, such as aldehydes, ketones and acids, by heating them to a high temperature, *e.g.* 280°, with hydriodic acid saturated at 0° and amorphous phosphorus. The above compounds are frequently converted in the first instance into the corresponding chlorides by means of phosphorus pentachloride.

4. By decomposing the zinc-alkyls with water (*Frankland*)—

$$Zn(C_2H_5)_2 + 2H_2O = Zn(OH)_2 + 2C_2H_6.$$

5. From hydrocarbons poorer in hydrogen, *i.e.* unsaturated hydrocarbons (see these), by the addition of nascent hydrogen; *e.g.* ethane from ethylene or acetylene and hydrogen, either in presence of platinum black or by heating the mixture of gases to 400°–500°. Also by heating with hydriodic acid (see above, 3), or by addition of halogen or halogen hydride, and exchange of the halogen for hydrogen, according to 1. Thus:

$$C_2H_4 + H_2 = C_2H_6, \qquad \left\{ \begin{array}{l} C_2H_4 + HBr = C_2H_5Br, \\ C_2H_5Br + H_2 = C_2H_6 + HBr. \end{array} \right.$$
$$C_5H_{10} + 2HI = C_5H_{12} + I_2;$$

C. From acids containing more carbon, with separation of carbon dioxide. Thus, by heating acetate of calcium with soda-lime, methane and carbonic acid are formed:

$$CH_3COONa + NaOH = CH_4 + Na_2CO_3.$$

In the case of the acids of higher molecular weight, this separation of carbonic acid is conveniently effected by heating with sodium ethylate.

D. By the combination of two radicles containing a smaller number of carbon atoms.

1. By the action of sodium upon the alkyl iodide in ethereal solution (*Wurtz*), see p. 17; or by heating with zinc in a sealed tube (*Frankland*):

$$2CH_3I + Na_2 = C_2H_6 + 2NaI.$$

By this method also two different radicles can be combined, *e.g.* $C_2H_5I + C_4H_9I$ give $C_2H_5 + C_4H_9 = C_6H_{14}$, ethyl-butyl (*Wurtz'* "Mixed Radicles").

2. By the action of halogen alkyl upon zinc alkyl, whereby dissimilar radicles may also be united—

$$\begin{matrix} CH_3I \\ CH_3I \end{matrix} + Zn\begin{matrix} CH_3 \\ CH_3 \end{matrix} = ZnI_2 + 2CH_3 . CH_3.$$

3. By the electrolysis of acids of the acetic acid series, (*Kolbe*, 1848):

$$\begin{matrix} CH_3 - COOH \\ CH_3 - COOH \end{matrix} = \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} + 2CO_2 + H_2.$$

The hydrogen is here evolved at the negative pole, and the hydrocarbon and carbon dioxide at the positive.

Methane, CH_4, (*Volta*, 1778). *Occurrence.* As an exhalation from the earth's crust, more especially at Baku in the neighbourhood of the Caspian Sea (the "Holy Fire" of Baku); on the peninsula of Apscheron, where it is used for heating purposes in the Tartar village of Balachana; in North America, *e.g.* from the large gas wells at Pittsburg, such as the Burns well (see Ethane); in Italy; near Glasgow; in the exhalations from mud volcanoes, for instance, at Bulganak in the Crimea, where the gas is almost pure methane, (*Bunsen*), and so on.

As pit gas in mines, where it causes explosions.

As marsh gas, produced along with CO_2 and N by the decomposition of organic substances under water; further, by the fermentation of cellulose, *e.g.* by river mud, by means of Schizomycetes (fission-fungi).

It is also found in rock salt (the Knistersalz of Wieliczka), and in the human intestinal gases, (up to 57 per cent. CH_4 after eating pulse).

The illuminating gas obtained by the destructive distillation of coal contains about 40 per cent. methane.

Modes of preparation. 1. Methane is formed synthetically in an indirect manner by the union of carbon and hydrogen to acetylene at the temperature of the electric arc, the subsequent transformation of this into ethane, and of the latter into methane at a red heat, (*Berthelot*), thus:

$$C_2H_2 + 2H_2 = C_2H_6;\ C_2H_6 = CH_4 + C + H_2.$$

2. From carbon monoxide and hydrogen under the influence of electricity; $CO + 3H_2 = CH_4 + H_2O$.

3. By leading sulphuretted hydrogen and carbon bisulphide over red-hot copper; $CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$.

4. *Preparation* from acetic acid, (*Bunsen*). Sodium acetate is heated with baryta or, less advantageously, with soda-lime (cf. p. 46), ethylene, C_2H_4, and hydrogen (up to 8 per cent.), being formed at the same time. Acetic acid may also be made to yield methane by a process of fermentation. (B. **21**, Ref. 62).

5. Methane is obtained chemically pure from zinc methyl and water; also (see B, 1) by the reduction of methyl iodide, CH_3I, *e.g.* in alcoholic solution by means of zinc in the presence of precipitated copper, (the *Gladstone-Tribe* "Copper-zinc Couple"); * also by the backward substitution of chloroform, $CHCl_3$, or carbon tetrachloride, CCl_4.

Properties. Gas, Sp. Gr. 0·559 ($= \frac{16}{28 \cdot 87}$, see p. 10), condensable under a pressure of 140 atmospheres at 0°. Boils at − 164°, and solidifies at − 186°. Absorption coefficient in cold water about 0·05, in cold alcohol 0·5. Burns with a pale and only faintly luminous flame. Is decomposed by the electric spark into carbon and hydrogen. Splits up for the most part into its elements on being led through a red hot tube, but there are formed at the same time C_2H_6, C_2H_4, C_2H_2, and, in smaller quantity, C_6H_6, benzene, $C_{10}H_8$, naphthalene, and other products. The first three hydrocarbons just mentioned, ethane, etc., behave similarly.

Ethane, C_2H_6. *Occurrence.* In crude petroleum. Constitutes, for example, the gas of the Delamater gas well in Pittsburg, and is there utilized for technical purposes.

Preparation. By the electrolysis of acetic acid, (*Kolbe*, 1848), and therefore formerly called "methyl"; also from ethyl iodide, alcohol, and zinc dust, or from zinc ethyl, (*Frankland*), hence the name "ethyl hydride." "Ethyl hydride" and "methyl," which were formerly supposed by *Frankland* and *Kolbe* to be different substances, were proved to be identical by *Schorlemmer* in 1863 by their conversion into C_2H_5Cl, which results from both in exactly the same way.

* This is a special preparation of zinc coated with copper precipitated from a solution of copper sulphate, which acts much more energetically than zinc alone. (Ch. Soc. J. 1884. 154.)

Properties. Gas, condensable under a pressure of 46 atmospheres at 4°; somewhat more soluble than methane in water and alcohol. Burns with a faintly luminous flame.

Propane, C_3H_8. Present in crude petroleum, and liquid below −17°. *Preparation.* By the action of hydriodic acid on acetone or glycerine (*Berthelot*), thus:

$$\underbrace{C_3H_6O}_{\text{Acetone.}} + 2H_2 = C_3H_8 + H_2O;$$

$$\underbrace{C_3H_8O_3}_{\text{Glycerine.}} + 3H_2 = C_3H_8 + 3H_2O;$$

or from isopropyl iodide with zinc and hydrochloric acid.

Butane, C_4H_{10}. Two isomeric butanes exist. Normal butane boils at +1°, and has the Sp. Gr. 0·60 at 0°; isobutane boils at −17°.

Normal butane, which is also present in petroleum, can be prepared by the action of sodium amalgam or zinc upon ethyl iodide, C_2H_5I, (*Frankland*), and has therefore the following constitution:

$$CH_3—CH_2—CH_2—CH_3 \text{ (di-ethyl)}:$$

$$\begin{matrix} CH_3—CH_2I \\ +CH_3—CH_2I \end{matrix} + Na_2 = \begin{matrix} CH_3—CH_2 \\ CH_3—CH_2 \end{matrix} + 2NaI.$$

Isobutane is formed from isobutyl iodide, C_4H_9I, (*Wurtz*), according to B, 1, and also by the action of zinc and water upon tertiary butyl iodide, (which see), (*Butlerow*).

Isomerism, Nomenclature, Constitution.

The *Isomerism* of the two butanes is explained on the assumption that in isobutane the carbon atoms are not combined with one another in a "continuous straight line" but in a "branching" one, according to the formula:

$$\begin{matrix} CH_3 \\ | \\ CH—CH_3, \\ | \\ CH. \end{matrix} = CH(CH_3)_3,$$

which corresponds with the name tri-methyl-methane. (See below.) The evidence for this rests upon the proof of the constitution of tertiary butyl iodide, C_4H_9I. (Cf. p. 51.)

These two butanes are theoretically the only possible ones of the formula C_4H_{10}.

All the succeeding hydrocarbons can, according to theory, exist in various isomeric modifications. Thus theoretically three pentanes should exist, and as a matter of fact three are known. Of hydrocarbons with six carbon atoms, five isomers are possible, and they are all known. Of the nine possible heptanes, C_7H_{16}, the existence of five has already been proved.

The number of theoretically possible isomers increases very rapidly with increasing carbon, so that, according to *Cayley*, 802 isomeric hydrocarbons of the formula $C_{13}H_{28}$ are possible.

Of these isomers only one can be **normal**, *i.e.* can have a carbon chain in a continuous straight line (p. 44), in which each of the two carbon atoms at either end are combined with three atoms of hydrogen, and all the middle ones with two, according to the formula:

$$CH_3—(CH_2)_n—CH_3.$$

A convenient *Nomenclature* for the more complicated paraffins is arrived at by making methane the starting point for all of them, that carbon atom from which the branching chain emanates being considered as originally belonging to CH_4, in which the hydrogen atoms are supposed to be wholly or partially replaced by hydrocarbon radicles, thus:

$$CH\begin{cases}CH_3\\CH_3\\C_2H_5\end{cases} = \text{Dimethyl-ethyl-methane.}$$

The names of the well known lower hydrocarbon radicles (alkyls) are also frequently used as a basis; for instance, the group $(CH_3)_2CH$ is termed isopropyl, (see Iso-propyl Alcohol), hence the compounds:

$$\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2—CH_3: \text{ Ethyl-isopropyl.}$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH<\begin{matrix}CH_3\\CH_3\end{matrix}: \text{ Di-isopropyl.}$$

Schorlemmer distinguishes between the following four classes of paraffins:—

1. Normal paraffins.*
2. Iso-paraffins, in which one assumes a single branching in the molecule.
3. Meso-paraffins, with several of such branchings.
4. Neo-paraffins, containing one carbon atom to which four others are united.

The boiling points of the normal hydrocarbons are always higher than those of the isomers; indeed the boiling point becomes lowered continuously the more the carbon atom chain is branched, *i.e.* the more methyl groups are gathered together in the molecule.

The *Constitution* of the higher paraffins can in most cases only be arrived at with certainty from their synthetical formation (*e.g.* normal butane and hexane), or from their chemical relation to oxygenated derivatives whose constitution is already known, especially to the ketones and acids. (See Ketones.)

If, for instance, by the action of PCl_5 upon acetone, for which the constitution $CH_3—CO—CH_3$ is proved, the substance $(CH_3)_2CCl_2 = CH_3—CCl_2—CH_3$ (acetone chloride) be formed, and this be then treated with zinc methyl, the resulting hydrocarbon, a pentane, will have the constitution $(CH_3)_4C$:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\Cl\end{matrix} + \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!Zn = \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} + ZnCl_2.$$

The same hydrocarbon, tetra-methyl-methane, is also produced by the action of zinc methyl on tertiary butyl iodide (see this and also p. 75), from which it follows that the constitution of the last named compound is $(CH_3)_3CI$:

$$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>\!CI + zn^{\dagger}CH_3 = \begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!>\!C—CH_3 + znI.$$

* In the case of the normal hydrocarbons the *official name* (p. 28) is the same as that hitherto in use. In the case of those with branching chains the longest normal chain gives the name, the branches being regarded as substituents, and the position of substitution being indicated by the successive numbering of the atoms of the carbon chain (the carbon atom which is nearest to the point of ramification is numbered 1; should there be more than one branching—say, a longer and a shorter—then No. 1 begins with the end carbon atom which stands nearest to the shorter branching). Trimethyl-methane is therefore called 2-methyl-propane; dimethyl-ethyl-methane, 2-methyl-butane; and tetramethyl-methane, 2-dimethyl-propane.

† $zn = \frac{1}{2}Zn$.

And, since tertiary butyl iodide is converted by nascent hydrogen into isobutane, the formula of the latter is thus proved to be $(CH_3)_3CH$.

The same constitution-formula for tertiary butyl iodide is arrived at from that of tertiary butyl alcohol. (See these.)

Pentanes. According to theory, and also in reality, three isomeric pentanes exist. (See table.)

1. *Normal pentane*, $CH_3—CH_2—CH_2—CH_2—CH_3$.
2. *Isopentane*, "O.N." *2-methyl-butane*, "*ethyl-isopropyl*," $(CH_3)_2=CH—CH_2—CH_3$ (from iso-amyl iodide).
3. *Tetra-methyl-methane*, "O.N." *2-dimethyl-propane* $C(CH_3)_4$.

The two first are contained in petroleum. (That portion of the petroleum distillate which boils under 0° is used as an anaesthetic under the names rhigolene and cymogene, and also in the preparation of ice.) Isopentane is formed from amyl iodide, according to B, 1; tetra-methyl-methane from acetone chloride or tertiary butyl iodide (p. 51).

Hexanes, C_6H_{14}. The five hexanes known boil between 46° and 71°. *Normal hexane* is produced, among other methods, by the action of hydriodic acid upon mannite, $C_6H_{14}O_6$, and also upon aniline, C_6H_7N. Its constitution follows from its formation from normal propyl iodide, $CH_3.CH_2.CH_2I$, and sodium, in a manner analogous to that of normal butane.

Normal heptane, C_7H_{16}, B.Pt. 98°, is present, for instance, in the ethereal oil of Pinus Sabinia, the Californian nut pine. It has a strong smell of oranges and produces insensibility when breathed.

From petroleum have been separated the two first-mentioned pentanes, n-hexane and an isomer, and n-heptane, all these being present in the so-called "gasoline," which is obtained by the distillation of petroleum, and is used for carbonizing coal-gas; further, **normal Heptane, n-Octane,*** **n-Nonane,** and **n-Decane,** besides an isomer of each, and in addition to these (as also from the distillation of cannel and Boghead coal), a large

* The petroleum ether and ligroïn of commerce consist principally of the hydrocarbons C_6H_{14}, C_7H_{16}, and C_8H_{18}.

number nominally of the higher hydrocarbons (*Cahours*, *Pelouze*, *Warren*, *Schorlemmer*).

In all probability these products are not chemical individuals but an inextricable mixture of homologues and isomers standing very near to each other, as is shown by a comparison with the artificially prepared normal hydrocarbons. (See below.)

F. Krafft has prepared those normal hydrocarbons from $C_{11}H_{24}$ to $C_{35}H_{72}$, which are mentioned on the table on p. 42, from the acids C_{12}, C_{14}, C_{16} and C_{18} of the acetic acid series (see these), for which the normal constitution, *i.e.* non-branching carbon chain, has been demonstrated; and also from the ketones, $C_nH_{2n}O$, which are obtained by subjecting the barium salts of these acids to dry distillation, either alone or together with acetate or heptoate of calcium, and which, as a consequence of their mode of formation, yield normal hydrocarbons. (See Ketones.) *Krafft* has further isolated the normal hydrocarbons $C_{17}H_{36}$ to $C_{23}H_{48}$, also $C_{24}H_{50}$, $C_{26}H_{54}$, and $C_{28}H_{58}$, by subjecting the paraffin obtained from lignite to fractional distillation *in vacuo*.

These are, from about $C_{16}H_{34}$ (M. Pt. 18°) on, solid at the ordinary temperature. Upon distillation under the atmospheric pressure, the higher hydrocarbons partially decompose into lower ones of the formulae C_nH_{2n+2} and C_nH_{2n}*, but they may be distilled in a vacuum, whereby their boiling points are reduced by 100° or more. (See table.)

Hexacontane, $C_{60}H_{122}$, has been prepared according to method of formation D. 1, p. 46, by the action of sodium upon myricyl iodide (from myricyl alcohol). It is interesting on account of the exceptional length of its carbon atom chain, and also because its production in this way shows to what an extent the above synthetic mode of formation may be carried.

Petroleum, *Earth Oil.*—This is produced by the decomposition of animal or vegetable organisms (*Engler*, B. **21**, 1816). It is found between Pittsburg and Lake Erie in America; between Lake Erie and Lake Huron in Canada; in Hanover, Holstein, and Elsass in Germany; in Boryslaw by Drohobycz in Galicia; in the Crimea; in the Caucasus, etc.

The specific gravity of the Pennsylvanian oil, after purification by

* The hydrocarbons undergo a similar decomposition upon treatment with $Al_2Br_6 + HI$; *e.g.* C_8H_{18} yields C_4H_8 and C_2H_5Br.

treatment with caustic soda and sulphuric acid and subsequent distillation, is 0·79 to 0·81, and its boiling point 200°–300°. The Canadian oil has a higher specific gravity, and contains substances of a very unpleasant odour. Petroleum has been a commercial product since 1848.

It must not be forgotten that all earth oils do not possess a similar composition. While the American oil consists almost entirely of paraffins, recent investigations have shown that petroleums from other sources, especially those from the Caucasus and Galicia, contain for the most part other hydrocarbons, the "naphthenes" (C_nH_{2n}, see p. 55; also J. pr. Ch. **43**, 561).

Crude earth oils also contain sulphur compounds, which give them an unpleasant odour (cf. B. **22**, 3303), organic acids (B. **23**, 867), etc.

Paraffin, obtained by *Reichenbach* in 1830 from wood tar, is got by the distillation of lignite or peat. It also is a mixture of many hydrocarbons, about 40 per cent. of it consisting of the compounds $C_{22}H_{46}$, $C_{24}H_{50}$, $C_{26}H_{52}$, and $C_{28}H_{58}$.

Liquid Paraffin (*Reichenbach's* "Eupion") and the butter-like **Vaseline** are high-boiling distillation products of lignite or petroleum, and the same applies to many lubricating oils.

Ozokerite, green, brown, and red, and of the consistency of wax, melting point 60°–80°, is a natural paraffin found at Boryslaw in Galicia, at Tscheleken near Baku (also called Neftgil), on the Caspian Sea, and forms the **ceresine** of commerce when bleached. From it there has been isolated a hydrocarbon "lekene" containing 24 atoms of carbon.

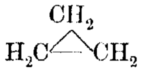
Asphalt, or **Earth Pitch,** found in India, Trinidad, Java, and Cuba, is a transformation product of the higher-boiling earth-oils, produced by the action of the oxygen of the air just as paraffin absorbs oxygen and becomes brown upon prolonged heating in the air. It is used for cements and salves, and in asphalting, photo-lithography, etc.

B. Olefines or Hydrocarbons of the Ethylene Series (Alkylenes): C_nH_{2n}.

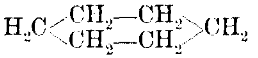
There are two series of hydrocarbons of the general formula C_nH_{2n}, the members of which differ from the corresponding paraffins by containing two atoms of hydrogen less in the molecule. The one series is that of the **Olefines**, of which ethylene, C_2H_4, is the first member; the other is that which contains **Tri-methylene, Tetra-methylene, Hexa-methylene,** etc.

The properties exhibited by these two series are so different that different constitutions must be accorded to them. The

olefines form addition-compounds with exceptional facility, being thus converted into the paraffins or their derivatives; from this the conclusion is drawn that, like the latter, they contain an open carbon chain. Tri-methylene, hexa-methylene, etc., show, on the contrary, no tendency (or at least only the very slightest) to pass into paraffins by taking up hydrogen or halogen, etc., their molecule being very stable. It will be shown later on that they contain not an open but a closed carbon chain, in which the carbon atoms are severally linked to one another in the same way, the chain therefore containing no first or last member, thus:—



Tri-methylene ("O.N." *Cyclo-propane*).



Hexa-methylene ("O.N." *Cyclo-hexane*).

These latter hydrocarbons are more or less related to the benzene derivatives, and will be treated of partly along with these, and partly in a separate section (XV.), as compounds midway between those of the fatty and the aromatic series. The naphthenes, mentioned on p. 54, belong to them.

Summary.

	*	M. Pt.	B. Pt.			M. Pt.	B. Pt.
Ethylene,	C_2H_4	−160°	−103°	Dodecylene,	$C_{12}H_{24}$	−31°	{96°†
Propylene,	C_3H_6		Gas	Tridecylene,	$C_{13}H_{26}$		233°
Butylene (3),	C_4H_8 α		−5°	Tetradecylene,	$C_{14}H_{28}$	−12°	{127°
	β		+1°	Pentadecylene,	$C_{15}H_{30}$		247°
	γ		−6°	Hexadecylene, (Cetene),	$C_{16}H_{32}$	+4°	274° {155°
Amylene (5),	C_5H_{10}*		+35°				
Hexylene,	C_6H_{12}		68°	Octadecylene,	$C_{18}H_{36}$	18°	{179°
Heptylene,	C_7H_{14}		98°	Eicosylene,	$C_{20}H_{40}$		
Octylene,	C_8H_{16}		124°	Cerotene,	$C_{27}H_{54}$	58°	
Nonylene,	C_9H_{18}		153°	Melene,	$C_{30}H_{60}$	62°	
Decylene,	$C_{10}H_{20}$		172°				
Undecylene,	$C_{11}H_{22}$		195°				

A **Methylene,** $CH_2=$, does not exist.

* The melting and boiling points given from C_5H_{10} on, are those of the normal hydrocarbons.

† { Signifies boiling point under 15 m.m. pressure.

The members of this second series of hydrocarbons differ from the paraffins by containing two atoms of hydrogen less than these.

In their physical properties they resemble the methane homologues very closely. C_2H_4, C_3H_6, and C_4H_8 are gases, C_5H_{10} a volatile liquid, the higher members liquids with rising boiling point and diminishing mobility, while the highest are solid and similar to paraffins. The boiling points of members of both series containing the same number of carbon atoms, and whose constitutions are comparable, lie very close together, but the melting points of the olefines are somewhat the lower of the two; *e.g.* $C_{16}H_{34}$, M. Pt. 21°, B. Pt. {157°, and $C_{16}H_{32}$, M. Pt. 4°, B. Pt. {155°.*

Most of the olefines are easily soluble in alcohol and ether, but *insoluble in water, only the lower members dissolving* slightly in the latter. The specific gravities of the normal olefines, measured at the melting points, rise from about 0·63 upwards, and approach with increasing carbon to a definite limit, viz., about 0·79.

In their chemical relations, the olefines differ materially from the paraffins:

(*a*) By additive reactions. They combine readily with nascent hydrogen, with hydrochloric, hydrobromic, and hydriodic acids, with chlorine, bromine, iodine, fuming sulphuric acid, hypochlorous acid, nitrous acid, and, generally speaking, with two monad atoms or monovalent groups, whereby members of the methane series or their derivatives ensue; hence their name of "Unsaturated Hydrocarbons."

$$C_2H_4 + H_2 = C_2H_6.$$
$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$
$$C_2H_4 + HI = C_2H_5I.$$
$$C_2H_4 + H_2SO_4 = C_2H_5(SO_4H).$$

Combination with hydrogen is sometimes effected, *e.g.* in the case of ethylene, by the aid of platinum black at the ordinary temperature, or by raising to a red heat, or by heating the olefines or their di-chlor-, etc., addition products with fuming hydriodic acid and phosphorus. (Cf. modes of formation of the saturated hydrocarbons B 1 and 5.)

Ethylene chloride, $C_2H_4Cl_2$, obtained by the combination of ethylene with chlorine, was formerly called the oil of the Dutch chemists, hence the name of "Olefines" for the whole class of hydrocarbons C_nH_{2n} (*Guthrie*).

Chlorine adds itself on more easily than iodine, but hydrochloric acid with more difficulty than hydriodic, bromine and hydrobromic acid standing mid-way. When a halogen hydride is used, the halogen attaches itself to that carbon atom which is combined with the least hydrogen. (Cf. Substitution Products.)

Particular olefines, *e.g.* isobutylene, also combine slowly with water to alcohols under the influence of dilute acids.

Ethylene combines with fuming sulphuric acid at the ordinary temperature, and with the English acid at 160°–170°.

Amylene forms with nitrogen tetroxide, N_2O_4, amylene nitrosate (A. **248**, 161); nitrogen trioxide and nitrosyl chloride also unite directly with the olefines.

(*b*) By their capability of polymerizing, especially in presence of sulphuric acid or zinc chloride.

In this way are formed from amylene, C_5H_{10}, in presence of sulphuric acid, the polymers $C_{10}H_{20}$, $C_{15}H_{30}$, and $C_{20}H_{40}$; and from tertiary butyl alcohol, warmed with acid of a definite strength, di-isobutylene. The polymerization is brought about through the junction of the atomic groups in question, by means of a new carbon-linking (see A. **189**, 44).

(*c*) By their behaviour upon oxidation. They are easily oxidized by $KMnO_4$ or CrO_3, but not by cold HNO_3.

By this reaction, either oxidation products—(acids)—containing less carbon are formed, by the breaking up of the double carbon bond (see p. 59, also A. **197**, 243); or, when $KMnO_4$ is employed, no carbon atoms are separated, but two hydroxyls are introduced, with formation of a diatomic alcohol. (See p. 202; cf. B. **21**, 1230, etc.)

The "official name" (p. 28) of the olefines is formed by replacing the last syllable "ane" of the paraffins by "ene." The position of the double bond is denoted by the number of the carbon atom from which it proceeds. In a branching chain the numbering is the same as in the case of the corresponding saturated hydrocarbons; in a normal chain it begins at the end carbon atom which is nearest to the double bond.

Modes of Formation. (*a*) Together with paraffins by the destructive distillation of many substances, such as wood, lignite and coal, and also by the distillation of the paraffins

(cf. pp. 45 and 52); illuminating gas consequently contains the olefines C_2H_4, C_3H_6, C_4H_8, etc.

(*b*) By abstraction of water from the alcohols, $C_nH_{2n+1}OH$, by heating them with sulphuric acid, phosphorus pentoxide, zinc chloride, etc. When sulphuric acid is used, an alkyl-sulphuric acid, *e.g.* ethyl-sulphuric acid, $C_2H_5SO_4H$, is first formed, and this decomposes upon further warming into alkylene and sulphuric acid. This method is especially applicable in the case of the lower homologues. Many alcohols split up into olefine and water, even when only strongly heated alone, *e.g.* secondary butyl alcohol at 240°.

A convenient method of obtaining the higher olefines is to distil the palmitic ethers of the higher alcohols under somewhat diminished pressure, when the corresponding olefines and palmitic acid are produced.

(*c*) By heating the halogen compounds $C_nH_{2n+1}X$ with alcoholic potash, or by passing their vapour over red-hot lime or hot oxide of lead, etc.; sometimes by distillation alone:

$$C_5H_{11}I + KOH = C_5H_{10} + KI + H_2O.$$

The bromine compounds are particularly suited for this.

(*d*) Sometimes from the haloid compounds $C_nH_{2n}X_2$ by abstraction of the halogen, *e.g.* ethylene from ethylene bromide by treatment with zinc, or zinc dust and alcohol:

$$C_2H_4Br_2 + Zn = C_2H_4 + ZnBr_2.$$

(*e*) By the electrolysis of dibasic acids of the succinic acid series; thus succinic acid itself yields ethylene:

$$C_2H_4(COOH)_2 = C_2H_4 + 2\,CO_2 + H_2.$$

Other modes of formation correspond with these under D. 1 and 2 for the paraffins.

Constitution of the Olefines. For ethylene, produced by the abstraction of two atoms of hydrogen from ethane, the following formulae may be given:

$$\text{I.}\ \begin{array}{l} CH_3 \\ | \\ CH{=} \end{array} \qquad \text{II.}\ \begin{array}{l} CH_2{-} \\ | \\ CH_2{-} \end{array} \qquad \text{III.}\ \begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$$

In the formulae I. and II., two free carbon affinities are assumed in the ethylene molecule. Formula III. follows from the assumption that the affinity which becomes free at each of

the two carbon atoms, upon abstraction of the hydrogen, is employed in creating a "double bond" between them.

Upon the taking up again of two atoms of hydrogen or halogen, the two free affinities in I. and II. would become bound by them, while in III. the double bond would be changed into a single one, and the free affinity of either carbon atom would be employed in binding the two new hydrogen (or other) atoms.

Now the ethylene bromide which is formed by the addition of bromine to ethylene has, for reasons which will be given under that compound, the constitution $CH_2Br—CH_2Br$, and likewise the compound obtained by the addition of ClOH, *i.e.* Cl and OH, viz. glycol chlorhydrin, the constitution $CH_2Cl—CH_2OH$; consequently formula I., according to which these substances would have the constitutions $CH_3—CHBr_2$ and $CH_3—CHCl(OH)$, is excluded.

Formula III. is more probable than formula II.:—

(*a*) On account of methylene, $CH_2=$, being incapable of existence; all attempts to isolate it have only yielded ethylene, C_2H_4 (see p. 60), so that free affinities probably cannot exist in the carbon atom.

(*b*) Because one would otherwise expect to have two isomeric ethylenes, but all endeavours to prepare an isomer have proved fruitless (*Tollens* and *L. Meyer*); and further, because more isomers of the next higher homologues, propylene and butylene, should exist than can actually be prepared.

(*c*) Because the free affinities to be assumed according to II. are never found singly (which should in that case be possible), but invariably in pairs only, and indeed only on neighbouring carbon atoms. This is proved from the constitution of the compounds obtained by the addition, for instance, of Br_2.

It is therefore to be concluded that in ethylene and its homologues a double carbon bond, corresponding to formula III., exists.

By this term "double bond" is not, however, to be understood a closer or more intimate combination. The olefines, on the contrary, are more readily oxidized than the paraffins, being thereby attacked at the point of

the double bond. Other properties, especially physical ones, also give indications that a double bond between two carbon atoms is looser, and therefore more easily broken than a single one. (Cf. *Brühl*, A. **211**, 162.)

---

1. A **Methylene** (*Methene*), CH_2, does not exist, as already mentioned on p. 59. Numerous attempts at preparing it, *e.g.* by the withdrawal of hydrogen and chlorine from methyl chloride, have invariably yielded ethylene, thus:—

$$2\,CH_3Cl - 2\,HCl = C_2H_4.$$

Here the two resulting CH_2-residues have united together, in the same way as the two methyl-groups coalesced to ethane (p. 46).

2. **Ethylene** (*Ethene*), *elayl, oil-forming Gas*, C_2H_4, $= CH_2{=}CH_2$. This compound was discovered in 1795 by four Dutch chemists. Its formula was established by *Dalton*.

Formation — see above. Illuminating gas generally contains 4 to 5 p.c. of ethylene. The latter is usually prepared by heating alcohol with excess of concentrated sulphuric acid, with addition of sand, a mixture of equal portions of the two liquids being subsequently dropped into the evolution flask. Sulphur dioxide, etc., are produced at the same time by secondary reactions. Small quantities can be conveniently prepared from ethylene bromide and zinc. It is further formed (instead of its hypothetical isomer indicated above) by heating ethylidene chloride, CH_3-CHCl_2, with sodium.

Liquid at 0° under 44 atmos. pressure. B. Pt. − 103°; M. Pt. − 160°. Very slightly soluble in water and alcohol. Burns with a luminous flame, and forms an explosive mixture with oxygen. When rapidly mixed with two volumes of chlorine and set fire to, it burns with a dark red flame, with formation of hydrochloric acid and deposition of much soot. It is converted at a red heat into methane, CH_4, ethane, C_2H_6, acetylene, C_2H_2, etc., with separation of carbon. (See p. 48.) It combines with hydrogen in presence of spongy platinum to ethane, C_2H_6.

3. **Propylene** (*Propene*), C_3H_6, $= CH_2{=}CH{-}CH_3$. Only one propylene belonging to the olefine group is theoretically possible and only one is known, viz. a methylated ethylene (see p. 54). (On the assumption of two free affinities instead of a double bond, four isomeric propylenes would be possible.) It

can be prepared from isopropyl iodide and caustic potash, or by heating glycerine with zinc dust. It is still a gas at $-40°$. Is isomeric with tri-methylene (see Section XV.)

4. **Butylene**, C_4H_8. Three butylenes are possible according to theory, and three are known. All of them are gaseous, their boiling points lying between $-6°$ and $+3°$. Butylene and pseudo-butylene are derived from normal butane, while isobutylene comes from isobutane, since they severally combine with H_2 to form these hydrocarbons. The first, α-butylene, is prepared from normal; the second, β-butylene, from secondary; and the third, γ-butylene, from tertiary butyl iodide, by the action of caustic potash upon these; the last can also be got from isobutyl alcohol and sulphuric acid. The isomerism of the two butylenes derived from normal butane is explained by the assumption of a double bond at different points, thus:

$CH_2{=}CH{-}CH_2{-}CH_3$	$CH_3{-}CH{=}CH{-}CH_3$
α-Butylene (1-*Butene*).	β-Butylene (2-*Butene*).

Isobutylene has the formula $(CH_3)_2{=}C{=}CH_2$ (2-*methyl*-2-*propene*). The behaviour of these isomers upon oxidation is in accordance with the above formulae, the oxidation always taking place at the point of the double bond.

The butylenes are isomeric with tetra-methylene (*cyclo-butane*, p. 323).

5. **Amylene**, C_5H_{10}. A large number of isomeric amylenes are known, among them being **Amylene** (B. Pt. 35°), which is obtained together with an isomer, Iso-amylene, by heating ordinary amyl alcohol with chloride of zinc. For it the constitutional formula $(CH_3)_2C{=}CH{-}CH_3$ (= trimethyl-ethylene) is assumed. This is known in the pure form under the name of "pental."

Another isomer is penta-methylene (*cyclo-pentane*, p. 323).

6. **Di-isobutylene**, C_8H_{16}. Formation, see above, B. Pt. 102°.

The higher Olefines of normal constitution, with 12, 14, 16 and 18 atoms of carbon, have been prepared by *Krafft* according to method *b*.

Cerotene and Melene (M. Pt. 62°) are obtained by the distillation of Chinese wax and bees' wax respectively. They are like paraffin in appearance, and are but slightly soluble in alcohol.

C. Hydrocarbons, C_nH_{2n-2}: Acetylene Series.

Summary.

		B. Pt.			M. Pt.	B. Pt.
C_2H_2	Acetylene (Ethine),	Gas.	$C_{12}H_{22}$	Dodecylidene (norm.),	-9°	105°†
C_3H_4	Allylene (Allene),	,,	$C_{14}H_{26}$	Tetradecylidene (norm.),	+6°	134°
C_4H_6	Crotonylene, etc. (Butine),	18°*	$C_{16}H_{30}$	Hexadecylidene norm.) (Cetine),	20°	160°
C_5H_8	Valerylene, etc. (Pentine),	51°	$C_{18}H_{34}$	Octadecylidene (norm.),	30°	184°
C_6H_{10}	Diallyl (Hexine),	59° 80°	$C_{20}H_{38}$	Eicosylidene (norm.),	liquid	314°
C_7H_{12}	Heptine, etc.,	108°				

* The boiling points from C_4 on, are those of the normal compounds.
† Boiling point under 15 m.m. pressure.

The hydrocarbons of this series again differ from those of the preceding by containing two atoms of hydrogen less. In physical properties they closely resemble both the latter and those of the methane series; thus the lowest members up to C_4H_6 are gaseous, the middle ones liquid, and the highest solid, and in their melting and boiling points they do not differ to any extent from those of the other series with an equal number of carbon atoms. The specific gravities of the normal hydrocarbons C_{12}, C_{14}, C_{16} and C_{18}, at the melting point, gradually approach with increasing carbon to a definite limit (0·80), and are somewhat higher than those of the corresponding members of the ethylene series throughout.

In their chemical relations the acetylenes stand nearer to the olefines than to the paraffins, in so far that they are unsaturated and therefore capable of forming addition products.

1. They combine either with two atoms of hydrogen or

halogen, or with one molecule of halogen hydride to olefines or their substitution products, thus:

$$C_2H_2 + H_2 = C_2H_4.$$
$$C_2H_2 + HBr = C_2H_3Br \text{ (vinyl bromide)};$$

or with four atoms of hydrogen or halogen, or two molecules halogen hydride to paraffins or paraffin substitution products, thus:

$$C_2H_2 + 2H_2 = C_2H_6 \text{ (in presence of platinum black)}.$$
$$C_2H_2 + 2HBr = C_2H_4Br_2.$$
$$C_2H_2 + 2Br_2 = C_2H_2Br_4.$$

Like many of the olefines, various members of this series combine with water under the influence of dilute acids, thus allylene, C_3H_4, gives acetone, C_3H_6O; and acetylene, C_2H_2, gives crotonic aldehyde, with intermediate formation of acetic aldehyde; and, as in the case of the olefines, ether-sulphuric acids are to be assumed here as intermediate products. $HgCl_2$ and other mercury salts also induce such hydration:

$$C_2H_2 + H_2O = C_2H_4O \text{ (aldehyde)}.$$
$$C_3H_4 + H_2O = C_3H_6O \text{ (acetone)}.$$

2. The capability of undergoing polymerization is also peculiar to several of the acetylene hydrocarbons; thus, acetylene is transformed into benzene upon being led through a red-hot glass tube. This is an important synthesis of benzene: $3C_2H_2 = C_6H_6$.

At the same time the compounds C_8H_8, $C_{10}H_8$, etc., are formed. Similarly allylene, C_3H_4, gives mesitylene, C_9H_{12}, upon treatment with sulphuric acid and a little water. (See Benzene Derivatives.)

3. Acetylene and some of its homologues react even at the ordinary temperature, in a manner which is peculiar to them, with an ammoniacal solution of cuprous or argentic oxide, to form reddish-brown or yellow-white precipitates, *e.g.* C_2Cu_2; C_2Ag_2; C_3H_3Ag, which are explosive, and which are decomposable by acids, such as HCl, with regeneration of the hydrocarbon.

The hydrogen of acetylene can be replaced by potassium or sodium; thus, upon heating the former with sodium, the com-

pounds C_2HNa and C_2Na_2 are obtained. These are de-posable by water or acids with separation of acetylene.

All the hydrocarbons C_nH_{2n-2} do not, however, give such metallic compounds, but only the true homologues of acetylene, *i.e.* those which contain a triple bond. (See below.)

Constitution. Upon grounds similar to those which have already been explained under ethylene, the constitutional formula for acetylene, C_2H_2, is assumed to be $CH \equiv CH$, according to which the carbon atoms are joined together by a triple bond.

For a compound C_3H_4, there are therefore possible the two following constitutional formulae:

$CH \equiv C-CH_3$ (Allylene), and $CH_2=C=CH_2$ (Allene).

As a matter of fact two hydrocarbons C_3H_4 do exist, only one of which, allylene, yields metallic compounds. It is therefore to be considered the true homologue of acetylene, containing a triple bond, according to the first of the two above formulae, while to allene the second formula, with the two double bonds, is to be ascribed. The constitution of the tetra-bromo-propanes, which are formed from these by the addition of Br_4, agrees with this conception.

The capability of yielding metallic compounds is therefore contingent upon the presence of the group $-C \equiv CH$.

If the group $-C \equiv C-$ is linked on both sides to carbon atoms, it contains no hydrogen atom which is directly bound to carbon, and thus cannot form metallic compounds.

In the case of the higher homologues, isomerism may be due either to the difference in position of the triple carbon bond in the molecule, or to the presence and different positions of the two double bonds. The constitution of a compound is fixed by the formation or otherwise of metallic derivatives, and by its behaviour upon oxidation. (See Oxidation of the Butylenes, (p. 57.)

The "O.N." (p. 28) of the acetylene homologues proper, with a triple carbon-linking, ends in "ine;" that of the hydrocarbons with a double carbon-linking, in "diene."

Modes of formation. 1. Along with the hydrocarbons already described, by the distillation of wood, lignite, coal, etc.; thus illuminating gas contains acetylene, allylene, and crotonylene.

2. By treating the haloid, preferably the bromine, compounds $C_nH_{2n}X_2$ and $C_nH_{2n-1}X$ with alcoholic potash:

$$C_2H_4Br_2 = C_2H_3Br + HBr.$$
$$C_2H_3Br = C_2H_2 + HBr.$$

Further, from the unsaturated alcohols, $C_nH_{2n}O$, by the separation of the elements of water from them.

3. By electrolysis of the acids of the fumaric acid series (*Kekulé*).

Acetylene is further formed:

4. Certain acetylene hydrocarbons, $R—C{\equiv}C—CH_3$, when heated with sodium, pass into the sodium compounds of their isomers, $R—CH_2—C{\equiv}CH$; on the other hand, when the latter are warmed with alcoholic potash, the opposite reaction takes place (*Faworsky*, B. **20**, Ref. 781; **25**, Ref. 81; **25**, 2244).

5. From its elements, when an electric arc is caused to pass between two carbon poles in an atmosphere of hydrogen (*Berthelot*). (Cf. B. 23, 1637.)

6. By decomposing C_2Ca or C_2K_2 by water.

7. By the incomplete combustion of many carbon compounds, for instance, when the gas in a *Bunsen* lamp burns below.

8. From chloroform and sodium (or red-hot copper):

$$2CHCl_3 + 3Na_2 = CH{\equiv}CH + 6NaCl.$$

9. From ethane, ethylene and methane at a red heat, or by the action of the induction spark. (See pp. 48 and 60.)

Acetylene (*Ethine*), C_2H_2.—Was first obtained impure by *E. Davy* from CaC_2 in 1839, and pure by *Berthelot* in 1849. Illuminating gas contains 0·06 per cent. Is best prepared from ethylene bromide. It becomes liquid at 1° under a pressure of 48 atmospheres, burns with a luminous and very sooty flame, and has a peculiar disagreeable smell. Dissolves in its own volume of water and in six times its volume of alcohol. Is poisonous, combining with the haemoglobin of the blood. It is decomposed into its elements with detonation by explosive fulminate of silver, and also by the electric spark.

It combines with hydrogen to ethane, upon being heated with the latter in presence of platinum black, or to ethylene, upon treating its copper

compound with zinc and ammonia. A mixture of acetylene and oxygen explodes violently when a light is applied to it. Chromic acid oxidizes acetylene to acetic acid, and permanganate of potash to oxalic acid. It combines with nitrogen under the influence of the induction spark to hydrocyanic acid (see this), and detonates upon being mixed with chlorine, but *additive products*, *e.g.* $C_2H_2Cl_2$ can however be prepared. As little as $\frac{1}{200}$ milligramme of it can be detected by the formation of the dark-red copper compound C_2Cu_2. This latter explodes when struck, or when heated to a little over 100°.

Allylene ("O.N." *Propine*), C_3H_4, = $CH_3—C≡CH$, can be prepared from propylene bromide, $C_3H_6Br_2$, = $CH_3—CHBr—CH_2Br$. It resembles acetylene.

Allene ("O.N." *Propadiene*), $C_3H_4 = CH_2=C=CH_2$, is obtained by the electrolysis of itaconic acid. It is gaseous, and does not yield metallic compounds.

Crotonylene or *Butine*, $CH_2=CH—CH=CH_2$, is contained in illuminating gas, and can be prepared by the action of hydriodic acid upon erythrite; it is isomeric or identical with:—

Pyrrolylene ("O.N." 1·3—*Butadiene*), C_4H_6 = $CH_2=CH—CH=CH_2$, which can be prepared from pyrrolidine (see this; cf. also B. **18**, 2077).

Piperylene ("O.N." 1·4—*Pentadiene*), C_5H_8, = $CH_2=CH—CH_2—CH=CH_2$, is a hydrocarbon obtained from piperidine. (B. **16**, 2059.)

Isoprene, *Hemi-terpene*, *Valerylene*, C_5H_8, probably $CH_2=C(CH_3)—CH=CH_2$ (B. Pt. 37°), is closely related to the terpenes from which it results on heating, and into which it passes by polymerization.

Di-allyl or *Hexine*, C_6H_{10}, = $CH_2=CH—CH_2—CH_2—CH=CH_2$, is got from allyl iodide and metallic sodium; B. Pt. 59°. Has a penetrating ethereal and radish-like odour. Gives no metallic compounds.

Conylene, C_8H_{14} (probably Iso-propyl-piperylene), B. Pt. 125°, is prepared from conine. (B. **14**, 710.)

The **higher hydrocarbons** of this series, containing 12, 14, 16 and 18 atoms of carbon in the molecule, have been prepared by *Krafft* from the corresponding olefines, according to method 2.

Isomeric with these hydrocarbons are certain hydro-derivatives of aromatic hydrocarbons, *e.g.* tetra-hydro-xylene, C_8H_{14}; deca-hydro-naphthalene, $C_{10}H_{18}$. (See Aromatic Compounds.)

D. Hydrocarbons, C_nH_{2n-4} and C_nH_{2n-6}

Among the hydrocarbons still poorer in hydrogen may be mentioned—

a. C_nH_{2n-4}: **Pirylene**, C_5H_6 (from piperidine. B. **15**, 1024). The homologues of this have received the termination "one," *e.g.* Hexone.

b. C_nH_{2n-6}: **Di-acetylene** ("O.N." *Butadiine*), C_4H_2, = $CH≡C—C≡CH$. This is prepared by heating the ammonia salt of

di-acetylene-di-carboxylic acid (see this), with ammoniacal copper solution, whereby it is transformed into the Cu-compound of di-acetylene, and then warming this with potassium cyanide. It is a gas of a peculiar odour, which yields a violet-red copper compound and a yellow silver one, the latter exploding upon being rubbed, even when moist. (*Baeyer*, B. **18**, 2269.)

Di-propargyl ("O.N." 1·5-*Hexadiine*), $C_6H_6 = CH \equiv C—CH_2—CH_2—C \equiv CH$, is obtained by the addition of bromine, $2Br_2$, to di-allyl, C_6H_{10}, 4 molecules HBr separating; B. Pt. 85°. It gives copper and silver compounds, and takes up 8 atoms of bromine, etc. It possesses an especial interest from being isomeric with benzene.

Likewise isomeric with the latter is the hydrocarbon C_6H_6 ("O.N." **2·4**-*Hexadiine*), $CH_3—C \equiv C—C \equiv C—CH_3$. (B. **20**, R. 564.)

Tropilidene, C_7H_8, B. Pt. 114°, from Tropine. (A. **217**, 133.)

II. HALOID SUBSTITUTION PRODUCTS OF THE HYDROCARBONS.

(See Table, p. 69.)

A. Halogen Derivatives of the Paraffins.

General Properties.—Only a few of these compounds, *e.g.* CH_3Cl, C_2H_5Cl, and CH_3Br are gaseous at the ordinary temperature, most of them being liquid, and those with a very large number of carbon atoms in the molecule solid. Such also as contain a large number of halogen atoms, *e.g.* CI_4, C_2Cl_6, are solid; among these come first the iodine compounds which, under similar conditions, also possess considerably higher boiling points than the analogous bromine compounds, and these again higher than the chlorine ones; for instance, C_2H_5I, B. Pt. 72°, C_2H_5Br, B. Pt. 39°, and C_2H_5Cl, B. Pt. 12°. Under comparable conditions, the boiling points of the iodides lie, for each atom of halogen, about 50°, (40°–60°), and those of the bromides about 22°, (20°–24°), above those of the chlorides.

The lowest members of the series have, in the liquid form,

at first a higher specific gravity than water, *e.g.* CH_3I, Sp. Gr. 2·2, C_2H_5Br, Sp. Gr. 1·47. With increasing carbon, however, they become more like the paraffins, the influence of the halogen diminishing, and consequently lighter than water.

The halogen substitution products of the hydrocarbons are almost or quite insoluble in water, but easily soluble in, and therefore miscible to any extent with alcohol and ether, and also soluble in glacial acetic acid. They often possess a sweet ethereal odour, but this becomes less marked with diminishing volatility. Most of them are combustible; thus methyl- and ethyl chloride burn with a green-bordered flame, while ethyl iodide and chloroform can only be set fire to with difficulty. Many members of the series containing 1 or 2 atoms of carbon produce insensibility and unconsciousness when inhaled, *e.g.* $CHCl_3$, $C_2H_3Cl_3$, C_2H_5Br, and C_2HCl_5.

In all these compounds the halogen is more firmly bound than in inorganic salts, so that, for instance, when silver nitrate is added to an alcoholic solution of the chlorine compound, *e.g.* chloroform, it causes no precipitation of AgCl. Nevertheless, the halogen is in most cases easily exchangeable for other elements or groups, a circumstance of the utmost importance for many organic reactions. This is especially true for the iodine and bromine compounds, which react more readily than the chlorides, and, on account of their lesser volatility, are easier to work with; thus C_2H_5Br reacts with $AgNO_3$ at the boiling temperature, and C_2H_5I in the cold even.

In all halogen compounds, the halogen can be again replaced by hydrogen by backward substitution, *e.g.* by Na-amalgam, by zinc dust and hydrochloric or acetic acid, or by heating with hydriodic acid. (See p. 44, B, 1.)

Of fluorine compounds, only a few are known as yet; CH_3F and C_2H_5F are gases.

Modes of formation.—1. By **Substitution.** Chlorine and bromine act for the most part as direct substituents, (see p. 43.) With the gaseous hydrocarbons their action even in the cold is an extremely energetic one, (*e.g.* chlorine mixed with methane easily causes an explosion, so that dilution with CO_2 is necessary): the higher members require to be heated.

HALOID SUBSTITUTION PRODUCTS OF THE HYDROCARBONS.

Methane Series. Mono-derivatives.	B. Pt.	Bi-derivatives.	M. Pt.	B. Pt.	Ethylene Series.	B. Pt.
CH_3Cl, Methyl chloride, - -	-22°	CH_2Cl_2, Methylene chloride		42°	C_2H_3Cl, Vinyl-chloride (chloro-ethylene), - -	-18°
CH_3Br, Methyl bromide, - -	+4°	CH_2Br_2, Methylene bromide,		97°		
CH_3I, Methyl iodide, - - -	44°	CH_2I_2, Methylene iodide, -	+4°	180°		
		$C_2H_4Cl_2$, $-Br_2$, $-I_2$, two isomers of each, - -			C_2H_3Br, Vinyl bromide, - - - -	23°
C_2H_5Cl, Ethyl chloride, - -	12°	Ethylene chloride, - - -		84°	C_2H_3I, Vinyl iodide.	56°
C_2H_5Br, Ethyl bromide, - -	39°	Ethylidene chloride, - -		57°	C_3H_5Cl, Allyl chloride, - - -	46°
C_2H_5I, Ethyl iodide, - - -	72°	Ethylene bromide, - - -	+9°	131°	C_3H_5Br, Allyl bromide, - - -	70°
		Ethylidene bromide, - -		108°		
C_3H_7Cl, $-Br$, $-I$, 2 isomers of each, *e.g.* Normal propyl iodide, - -	102°	Tri-derivatives.			C_3H_5I, Allyl iodide.	101°
Iso-propyl iodide,	89°	$CHCl_3$, Chloroform, - -	-70°	61°	$C_2H_2Cl_2$ Di-chloro-ethylene. - - -	55°
C_4H_9Cl, $-Br$, $-I$, 4 isomers of each, *e.g.*		$CHBr_3$, Bromoform, - - -	+2°	151°	C_2HCl_3, Tri-chloro-ethylene, - - -	88°
1. Normal primary,	130°	CHI_3, Iodoform, - - - -	119°	subl.		
2. Iso-primary,	120°	$C_2H_3Cl_3$, Methyl chloroform,		74°	C_2Cl_4, Tetra-chloro-ethylene, - - -	121°
3. Secondary,	117°	$C_3H_5Cl_3$, Tri-chlorhydrin, -		158°		
4. Tertiary Butyl iodide, - -	98°	Higher Substitution Products.			Acetylene Series.	
$C_5H_{11}Cl$, Iso-amyl chloride, -	101°	CCl_4, Carbon tetra-chloride,		77°	C_2HCl, Mono-chlor-acetylene, - -	Gas.
$C_5H_{11}I$, Iso-amyl iodide, - -	147°	CI_4, Carbon tetra-iodide (solid), - - - - - -		decomp.	C_2HBr, Mono-brom-acetylene, - -	Gas.
$C_6H_{13}Cl$, Hexyl chloride, etc.	126°	C_2Cl_6, Perchloro-ethane, -	160°	182°		

The first halogen atom enters most easily into the compound, the substitution becoming more difficult as the number of those atoms present increases. In the case of the higher hydrocarbons there usually result two isomeric mono-substitution products. The action of the halogens is further facilitated by sunlight, and by the presence of iodine, this latter acting as a carrier of chlorine by the alternate formation of ICl_3 and ICl, thus: $ICl_3 = ICl + Cl_2$. Antimony pentachloride and ferric chloride act in the same way (and also for brominating and iodating,—B. **18**, 2017; A. **231**, 195); iron wire is especially useful in brominating (B. **24**, 4249). When it is wanted to chlorinate completely, the substance in question is repeatedly saturated with chlorine in presence of iodine, and heated in a tube to a high temperature.

From methane are formed the whole series of substitution products up to CCl_4.

Ethane first yields ethyl chloride, C_2H_5Cl, then ethylene chloride, $C_2H_4Cl_2$ and so on up to C_2Cl_6.

From propane is first produced normal propyl chloride, C_3H_7Cl, and finally C_3Cl_8. The latter decomposes, upon vigorous chlorination, first into C_2Cl_6 and CCl_4, and the perchloro-ethane subsequently into 2 molecules CCl_4. On chlorinating butane and the higher hydrocarbons strongly, an analogous splitting up of the molecule is effected. Strong chlorination or bromination readily gives rise at the same time to hexachloro- or hexabromo-benzene.

Iodine seldom acts as a direct substituent, since by this reaction hydriodic acid would be formed, which would then substitute backwards. (See p. 45.) To induce the action therefore, the HI formed must be removed by HIO_3 or HgO. The iodine substitution products of the hydrocarbons are usually prepared indirectly, (according to 2 or 3).

2. From **Unsaturated Hydrocarbons.** These combine readily with halogen or halogen hydride. (See p. 56.)

It stands to reason that no methane derivatives can be formed in this way.

Ethylene gives with hydrochloric, hydrobromic, and hydriodic acids, ethyl chloride, etc., *i.e.* mono-substitution products of ethane; with chlorine, etc., it gives di-substitution products.

The compound $C_2H_4Cl_2$, obtained by the action of chlorine, is called ethylene chloride, and is isomeric with the ethylidene chloride got by the further chlorination of C_2H_5Cl. (For an explanation of this isomerism, see p. 76.)

Propylene combines with hydriodic acid to isopropyl

iodide, C_3H_7I, which is reconverted into propylene by separation of HI. But the same propylene results from a compound isomeric with isopropyl iodide, viz., normal propyl iodide, (and also, of course, from the above-mentioned normal propyl chloride), by the splitting off of hydriodic (or hydrochloric) acid, so that by this reaction normal propyl iodide can be transformed into isopropyl iodide. (See p. 74.) From the three butylenes there result similarly two butyl iodides, viz., secondary and tertiary, which, as well as the two other existing butyl iodides, yield these butylenes again with alcoholic potash ; in this way the two last-mentioned butyl iodides are convertible into their isomers, the two first, (see p. 75).

A study of the constitution of the compounds formed, shows that in these addition reactions the halogen invariably affixes itself to that carbon atom with which are combined the smallest number of hydrogen atoms, *e.g.*

$$CH_3—CH{=}CH_2 + HI = CH_3—CHI—CH_3,$$
$$(\textit{not}\ CH_3—CH_2—CH_2I)\ ;$$

from C_3H_7X onwards therefore, there result only "secondary" and "tertiary"* compounds.

3. From **Compounds containing oxygen.**

(*a*) From the alcohols $C_nH_{2n+1}OH$. In these the OH is readily exchangeable for chlorine, bromine, or iodine by the action of halogen hydride,† thus :

$$C_2H_5OH + HBr = C_2H_5Br + H_2O.$$

In the action of these acids a state of equilibrium is reached, since the above reaction can go on in exactly the opposite direction ; it is therefore necessary either to use a large excess of halogen hydride, (*e.g.* to saturate with the gas or to heat in a sealed tube), or to remove the water formed, by sulphuric acid, zinc chloride, etc.

* The names "primary," "secondary," and "tertiary" compounds are founded upon those of the alcohols—primary, secondary and tertiary—in question, from which they can be prepared according to method 3, *a*.

† In such exchange the halogen takes the place of the hydroxyl, so that the constitution of the haloid product corresponds with that of the alcohol used.

Methyl- and ethyl chlorides are easily prepared by distilling the corresponding alcohol with common salt and sulphuric acid, or by leading hydrochloric acid gas into the warmed alcohol containing half its weight of zinc chloride in solution, (*Groves*).

The chlorides of phosphorus are also applicable for the substitution of OH by Cl, since they react in the same way with alcohols as with water, thus :

$$PCl_3 + 3HOH = P(OH)_3 + 3HCl.$$
$$PCl_3 + 3C_2H_5OH = P(OH)_3 + 3C_2H_5Cl.$$

Phosphorus pentachloride is most frequently used for this purpose, going as a rule into the oxychloride :

$$PCl_5 + C_2H_5OH = C_2H_5Cl + HCl + POCl_3.$$

Phosphorus oxychloride itself is also sometimes employed. Of especial importance here is the application of the halogen compounds of phosphorus in the production of bromine and iodine compounds. The former need not be prepared beforehand, the end being achieved by gradually bringing phosphorus and iodine or bromine together in presence of the alcohol :

$$3CH_3OH + P + 3I = 3CH_3I + H_3PO_3.$$

(*b*) From the polyatomic alcohols, halogen substitution products are also obtained, *e.g.* tri-chlorhydrin, $C_3H_5Cl_3$, from glycerine, $C_3H_5(OH)_3$, and PCl_5; isopropyl iodide, C_3H_7I, or allyl iodide, C_3H_5I, from glycerine and HI, *i.e.* I and P, according to the conditions of the experiment (see p. 74); hexyl iodide, $C_6H_{13}I$, from mannite, $C_6H_8(OH)_6$ and HI, the latter acting here as a reducing agent also.

(*c*) From aldehydes and ketones, (see these), di-chloro-substitution products result by the action of PCl_5, *e.g.* ethylidene chloride, $C_2H_4Cl_2$, from aldehyde, C_2H_4O; acetone chloride, $C_3H_6Cl_2$, from acetone C_3H_6O.

(*d*) Halogen substitution products are also occasionally prepared from acids by the exchange of O and OH for three Cl atoms.

4. Chlorine and bromine compounds are frequently formed from the corresponding iodine or bromine ones by driving out the weaker halogen from its combination by the stronger one, *e.g.* isopropyl bromide from the iodide, or methylene bromide from methylene iodide; (also by treatment with mercuric chloride, stannic chloride, or fuming hydrochloric acid). Conversely

the chlorine and bromine compounds may be transformed into the iodine ones by heating with sodium iodide (in alcoholic solution, see B. 18, 519), potassium iodide, dry calcium iodide (B. 16, 392), or with fuming hydriodic acid.

Fluorine compounds are obtained in a similar way from silver fluoride and carbon tetrachloride, chloroform, methylene chloride, or alkyl iodide.

5. **Carbon Tetrafluoride**, CF_4, also results from the direct union of carbon and fluorine.

6. For special modes of formation, see the compounds CH_3Cl, $CHCl_3$, and CHI_3.

Mono-substitution Products.

Methyl chloride,* CH_3Cl (*Dumas* and *Péligot*, from CH_4O, 1836). Prepared from methyl alcohol, $ZnCl_2$, and HCl (see p. 71); also by distilling the "vinasse" of the sugar manufactories, and heating the tri-methylamine hydrochlorate obtained to 260° (*Vincent*). Colourless gas with an ethereal odour. B. Pt. − 22°. Slightly soluble in water (4 volumes in 1 volume water), but more easily in alcohol. Is used for the production of artificial cold, for extracting perfumes from flowers, and for methylating dyes in the colour industry. Burns with a green-bordered flame.

Methyl bromide, CH_3Br (*Bunsen*, from cacodyl compounds, 1844). Prepared from methyl alcohol, P and Br. B. Pt. + 4·5°; Sp. Gr. 1·73 at 0°; has a pleasant ethereal odour similar to that of methyl chloride and of chloroform and a burning taste, and burns with difficulty, with a greenish-brown flame.

Methyl iodide, CH_3I (*Dumas* and *Péligot*). Prepared from methyl alcohol, P and I. B. Pt. 44°; Sp. Gr. 2·27 at 25°. Is not easily set fire to. When it is heated with 16 volumes of water to 100°, methyl alcohol and hydriodic acid are produced.

Ethyl chloride, C_2H_5Cl† (*Basilius Valentinus*: "Spiritus salis et vini," or "sweetened alcohol"). Prepared by the action of Cl on C_2H_6 (*Schorlemmer*; cf. pp. 48 and 70.) For *Groves'* method (1874), see p. 72. Is formed as a bye-product in the manufacture of chloral. Easily compressible gas; B. Pt. + 12°.

* "O. N." Chloro-methane. † "O. N." Chloro-ethane.

Burns with a green bordered flame. Can be easily preserved in alcoholic solution (1 : 2).

Ethyl bromide, C_2H_5Br (*Serullas*, 1827). Prepared from alcohol with P and Br, or with $KBr + H_2SO_4$. Burns with a beautiful green smokeless flame, emitting bromine vapours.

Ethyl iodide, C_2H_5I (*Gay-Lussac*, 1815). Is best prepared from 90 per cent. alcohol, P and I. Colourless liquid with a peculiar ethereal smell, somewhat resembling that of leeks. B. Pt. 72°; Sp. Gr. 1·94. Almost insoluble in water, but miscible with alcohol and ether, and difficult of ignition. Heated with water to 100°, it is converted, analogously to methyl iodide, into C_2H_6O and HI. Chlorine converts it into C_2H_5Cl, and bromine into C_2H_5Br. When exposed to light, iodine separates with formation of C_4H_{10}. It is used for inhalation in cases of asthma.

Ethyl Fluoride, C_2H_5F. A gas of ethereal odour, which liquefies at − 48°; it burns with a blue flame, and does not attack glass.

Of **Propyl chloride, -bromide,** and **-iodide,** C_3H_7X, two isomers each exist, the normal propyl and the isopropyl compounds, the former boiling at a somewhat higher temperature than the latter. To the normal compounds the constitutional formula $CH_3—CH_2—CH_2X$ is ascribed, and to the iso-compounds the formula $CH_3—CHX—CH_3$, since they are derivable respectively from normal propyl alcohol and from isopropyl alcohol or acetone, substances whose constitution is easily arrived at.

According to theory only these two cases are possible, since propane contains but two kinds of hydrogen atoms, viz.: (1) six combined with the end carbon atoms, and (2) two combined with the middle ones. For the transformation of the normal into the iso-compounds, see p. 70.

Normal propyl chloride, see p. 70, also table, p. 69.

Normal propyl bromide only passes partially into isopropyl bromide at 280°, but when heated with Al_2Br_6 the transformation is direct, an intermediate Al-compound being formed (*Kekulé, Schrötter*).

Isopropyl iodide* is prepared from glycerine, phosphorus and iodine (see p. 72); allyl iodide is formed as intermediate product, and at the same time some propylene:

$$C_3H_5(OH)_3 + 3HI - 3H_2O = C_3H_5I_3 = C_3H_5I + I_2.$$
$$C_3H_5I + HI = C_3H_6 + I_2. \quad C_3H_5I + 2HI = C_3H_7I + I_2.$$

* "O.N." 2-Iodo-propane.

Normal propyl iodide is got from the alcohol.

The **Butyl-haloid compounds**, C_4H_9X, are already known each in four isomeric forms, which in part differ materially from one another in boiling point (up to 30°).

As a matter of fact four isomers are theoretically possible. Thus from normal butane are derived:

(*a*) $CH_3—CH_2—CH_2—CH_2I$, and (*b*) $CH_3—CH_2—CHI—CH_3$.
Normal butyl iodide ("O.N." 1-*Iodo-butane*). (*Linnemann.*)
Secondary butyl iodide ("O.N." 2-*Iodo-butane*).

In these hydrocarbons also there are two kinds of hydrogen atoms, (*a*) those connected with the end, and (*b*) those with the middle carbon atoms.

From tri-methyl-methane, $CH\equiv(CH_3)_3$, are similarly derived

(*c*) $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2I$, and (*d*) $\begin{matrix}CH_3\\CH_3\end{matrix}>CI—CH_3$.
Isobutyl iodide.* (*Wurtz.*)
Tertiary butyl iodide.† (*Butlerow.*)

The constitution of these four compounds follows, among other reasons, from those of the four corresponding butyl alcohols, (p. 93), from which they can be prepared by the action of halogen hydride (HI).

As regards the transformation of *a* into its isomer *b*, and of *c* into *d*, see p. 71. Isobutyl bromide changes into the tertiary compound by simple heating to 230°-240°, which is to be explained by the intermediate formation of butylene.

The **Isobutyl compounds** are the easiest to prepare, (from isobutyl alcohol). The **Tertiary** readily react with H_2O to form the alcohol and halogen hydride, this taking place even in the cold in the case of the iodide. For the constitution of tertiary butyl iodide, see also p. 51.

Of the **Isomers**, $C_5H_{11}X$, *e.g.* **amyl chloride**, eight are theoretically possible. Six chlorides are actually known. Of special interest are **iso-amyl chloride, bromide**, etc., compounds which are obtained from iso-amyl alcohol, and to which the constitution $(CH_3)_2=CH—CH_2—CH_2X$ (2-*methyl*-4-*halogen-Butane*) is assigned.

Further, analogous compounds with from 6 to 12 and even more, *e.g.* 16 and 30, carbon atoms are known. A **secondary hexyl iodide**, $CH_3—(CH_2)_3—CHI—CH_3$, is got from mannite or dulcite with HI and P.

Cetyl bromide and **-iodide**, $C_{16}H_{33}Br$ and $C_{16}H_{33}I$, are liquids which solidify at a moderate temperature.

2. Di-substitution Products.

Methylene chloride, CH_2Cl_2, **Methylene bromide**, CH_2Br_2, and **Methylene iodide**, CH_2I_2, are colourless liquids which one obtains either from the tri-haloid substitution products

* "O.N." 2-Methyl-3-Iodo-propane. † "O.N." 2-Methyl-2-Iodo-propane.

by backward substitution, or from the mono-substitution products by the introduction of more halogen. (See table, p. 69).

The compounds $C_2H_4X_2$ are known in two isomeric forms, to which are assigned the constitutional formulae :

$CH_2X—CH_2X$	and	$CH_3—CHX_2$.
Ethylene compounds.		Ethylidene compounds.

The former result from the addition of halogen to ethylene, or from the action of halogen hydride or halogen phosphorus upon glycol, $C_2H_4(OH)_2$, (see this).

Ethylene chloride,* $C_2H_4Cl_2$, (oil of the Dutch chemists, 1795), B. Pt. 84°.

Ethylene bromide,† $C_2H_4Br_2$, (*Balard*), is prepared by leading ethylene into cold bromine, and has a pleasant odour like that of chloroform. M. Pt. +9° ; B. Pt. 131° ; Sp. Gr. > 2. Crystallizes in the cold. Yields glycol, $C_2H_4(OH)_2$, upon prolonged heating with excess of water to 100°, or with K_2CO_3.

Ethylene iodide, $C_2H_4I_2$, is solid and easily decomposable.

These compounds yield acetylene with alcoholic potash, and are transformed into glycol by exchanging their halogen atoms for hydroxyl. Now, from the relation of the latter to glycol chlorhydrin and mono-chloracetic acid, it has the constitution $\begin{matrix} CH_2—OH \\ \vert \\ CH_2—OH \end{matrix}$; consequently in ethylene chloride, etc., the two halogen atoms are combined with different atoms of carbon.

The following forms more special proof of the above statement: Ethylene chloride can, by exchange of Cl for OH, be transformed into glycol chlorhydrin, (which is also formed from glycol and HCl), and this can then be oxidized to mono-chloracetic acid,

$$C_2H_4(OH)Cl + O_2 = H_2O + CH_2Cl—COOH$$

(see this). Since in the latter the OH and Cl are bound to different carbon atoms, the same must be the case in glycol chlorhydrin, and also, for the Cl atoms, in ethylene chloride.

The **Ethylidene compounds** are obtained from aldehyde, (para-aldehyde), by exchange of the oxygen for halogen by means of phosphorus chloride, etc.

Ethylidene chloride, also called ethidene chloride,* is, however, most conveniently prepared with phosgene, $COCl_2$, thus:

$$CH_3-CHO + COCl_2 = CH_3-CHCl_2 + CO_2.$$

It is also formed by the further chlorination of C_2H_5Cl, and is a bye-product in the manufacture of chloral. Its boiling point (57°) is lower than that of ethylene chloride (84°). It is an anaesthetic.

Propylene chloride,† etc., $C_3H_6Cl_2$, $-Br_2$, $-I_2$, are likewise known. They result partly upon the addition of halogen to propylene, and have then an unsymmetrical constitution, *e.g.* propylene chloride, $CH_3-CHCl-CH_2Cl$. Isomeric with them are the symmetrically constituted **Trimethylene derivatives**, of which tri-methylene-bromide,‡ $CH_2Br-CH_2-CH_2Br$, results from the addition of hydrobromic acid to allyl bromide:

$$CH_2=CH-CH_2Br + HBr = CH_2Br-CH_2-CH_2Br.$$

Tetramethylene bromide, $CH_2Br-CH_2-CH_2-CH_2Br$. B. Pt. 189°.

Pentamethylene bromide, $CH_2Br-(CH_2)_3-CH_2Br$. B. Pt. 205°. (Cf. B. **22**, Ref. 489.)

3. Tri-substitution Products.

Chloroform, $CHCl_3$, (*Liebig* and *Soubeiran*, 1831; formula established by *Dumas*, 1835.)

Formation. 1. From methane and methyl chloride, (see p. 70). 2. By heating alcohol with chloride of lime and water. 3. Along with alkaline formate by warming chloral or chloral hydrate with aqueous alkali:

$$CCl_3-CHO + NaOH = CHCl_3 + HCO_2Na.$$

This last method of formation is the best for the obtaining of pure chloroform. Its formation from alcohol and bleaching powder, *i.e.* by the action of chlorine upon alcohol, may be considered to rest upon the intermediate production of chloral.

Properties. Colourless liquid of a peculiar ethereal odour and sweetish taste. Hardly soluble in water. Solid below −70°. B. Pt. 61·2°. Sp. Gr. 1·527. Dissolves fats, resins, caoutchouc, iodine, etc. Is a most valuable anaesthetic, (*Simpson*, Edinburgh, 1848).

The carbamine reaction (see Iso-nitriles) furnishes a delicate test for the presence of chloroform.

* "O.N." 1-Dichloro-ethane. † "O.N." 1-2-Dichloro-propane. ‡ "O.N." 1-3-Di-bromo-propane.

Reactions. Alkaline chromate produces phosgene. Potassium amalgam induces the formation of acetylene. Potash decomposes it to formate and chloride, thus:

$$CHCl_3 + 4KOH = HCO_2K + 3KCl + 2H_2O.$$

Ammonia at a red heat produces hydrocyanic and hydrochloric acids:

$$CHCl_3 + NH_3 = HCN + 3HCl.$$

Bromoform, $CHBr_3$, is sometimes present in commercial bromine.

Iodoform, CHI_3 (*Serullas*, 1822; formula established by *Dumas*), is prepared by warming alcohol with iodine and alkali or alkaline carbonate:

$$C_2H_5OH + 4I_2 + 6KOH = CHI_3 + HCO_2K + 5KI + 5H_2O.$$

It can also be got in the same way from acetone, aldehyde, lactic acid and, generally, from compounds which contain the group CH_3—CHOH—C, or CH_3—CO—C (*Lieben*); also by the electrolysis of an alcoholic solution of iodine.

Yellow hexagonal plates. M. Pt. 119°. Contains only 0·25 per cent. H, which at first caused the presence of the latter to be overlooked. Has a peculiar odour, and is volatile with steam. Important antiseptic.

Fluoroform, CHF_3. Gaseous (cf. p. 73).

Methyl-chloroform,* $CH_3 \cdot CCl_3$. This compound, the trichloride of acetic acid, also acts as an anaesthetic.

Glyceryl chloride,† *tri-chlorhydrin*, $C_3H_5Cl_3$, is obtained from glycerine and PCl_5 (p. 72). B. Pt. 158°. The corresponding bromine compound is also known, but not the iodine one, $C_3H_5I_3$, which decomposes in the nascent state (*i.e.* when glycerine, phosphorus and iodine react together), into allyl iodide, C_3H_5I, and I_2. (See pp. 72 and 74.)

4. Higher Substitution Products.

Carbon tetra-chloride, CCl_4. Can be prepared from chloroform or carbon bisulphide and chlorine. Colourless liquid. B. Pt. 77°.

Carbon tetra-bromide, CBr_4. Plates. Boils without decomposition.

Carbon tetra-iodide, CI_4. Dark red octahedra. Decomposes upon heating.

Carbon tetra-fluoride, CF_4. Colourless gas, readily condensible; can be synthetized from lampblack and fluorine.

Per-chloro-ethane, C_2Cl_6. Rhombic plates of camphor-like odour. Melts and boils at 185°.

B.—Haloid Derivatives of the Unsaturated Hydrocarbons.

These compounds are obtained either by partially withdraw-

ing halogen or halogen hydride from the halogen derivatives of the saturated hydrocarbons, or by incompletely saturating the hydrocarbons poorer in hydrogen with halogen or halogen hydride, *e.g.* $C_2H_4Br_2 - HBr = C_2H_3Br$. $C_2H_2 + HBr = C_2H_3Br$.

They are also got by treating the haloid addition products of unsaturated acids with potassium carbonate:—

$$C_4H_6Cl_2O_2 \quad = \quad C_3H_5Cl + HCl + CO_2.$$

Crotonic acid dichloride; α-Chloro-propylene.

The allyl compounds, C_3H_5X, result from allyl alcohol and halogen hydride or halogen phosphorus.

These unsaturated products are very similar to the corresponding saturated ones, but they are of course capable of combining further with halogen or halogen hydride, and they exist in geometrically isomeric modifications.

The following among them may be mentioned:—

Bromo-ethylene, *vinyl bromide*, C_2H_3Br, $= CH_2{=}CHBr$.

Allyl-chloride, -bromide, and -iodide,* $CH_2{=}CH{-}CH_2X$.

These are of importance on account of their relation to the allyl compounds found in nature, *e.g.* oil of mustard and oil of garlic. The iodide is prepared from glycerine, phosphorus and iodine, and from it, by means of $HgCl_2$, the chloride.

Isomeric with these are the **Propylene compounds**, *e.g.* **α-Chloro-propylene** ("O.N." 1-*chloro*-1-*propene*), $CHCl{=}CH{-}CH_3$. In its formation, as given above, both of the stereo-chemical isomers, which are theoretically possible, result (*Wislicenus*, A. **248**, 281), viz.:—

```
H—C—Cl              H—C—Cl
  ‖        and        ‖
H—C—CH3           CH3—C—H
```

α-Chloro-propylene; Iso-α-Chloro-propylene.

Per-chloro-ethylene, C_2Cl_4. Colourless liquid. B. Pt. 121°.

Mono-chlor-acetylene, C_2HCl. Gas which catches fire spontaneously.

Mono-brom-acetylene, C_2HBr. Also a spontaneously inflammable gas, which burns with a purple-coloured and exceedingly sooty flame.

Halogen compounds containing several different halogens are also known.

III. MONATOMIC ALCOHOLS.

As alcohols are designated those compounds containing oxygen and of neutral reaction, which, like bases, combine with acids with the elimination of water, to form other compounds analogous to salts in constitution, the latter being termed "esters," "ethers," or "compound ethers," thus:

$$C_2H_5OH + NO_2OH \; = \; C_2H_5.(O.NO_2) + H_2O.$$

Alcohols are further easily transformable by oxidation into

compounds richer in oxygen or poorer in hydrogen, (aldehydes, ketones, and acids); they do not undergo substitution by the action of halogens, but oxidation, etc., etc.

According to theory, the alcohols are derived from the hydrocarbons by the replacement of hydrogen by hydroxyl. (See pp. 27 and 82.)

Just as we know mono- and poly-acid bases, so are there mono-, di-, tri-, etc., hydric or -atomic alcohols, according to the number of molecules of a monobasic acid which can react with one molecule of the alcohol to form an ether. The poly-atomic alcohols, *e.g.* glycol, $C_2H_4(OH)_2$, glycerine, $C_3H_5(OH)_3$, mannite, $C_6H_8(OH)_6$, etc., will be treated of later on.

The monatomic alcohols are likewise either saturated or unsaturated, according to the hydrocarbons from which they are derived. The unsaturated resemble the saturated closely, excepting in that they are capable of forming addition compounds.

A. Monatomic Saturated Alcohols, $C_nH_{2n+1}OH$

(See Table, p. 81.)

The lowest members of this series are colourless mobile liquids, the middle ones are more oily, and the highest—from dodecyl alcohol, $C_{12}H_{25}OH$, onwards—are solid and like paraffin in appearance at the ordinary temperature. Gaseous alcohols are unknown. With analogous constitution the boiling point rises with tolerable regularity; in the case of the lower members by about 19°, and higher up in the series by a smaller number.

The lowest members are miscible with water, but this solubility rapidly diminishes as the series ascends; thus butyl alcohol requires 12 parts and amyl alcohol 40 parts of water for solution; while the higher members are no longer soluble in water. The former can be separated or "salted out" from their aqueous solution by the addition of salts, *e.g.* K_2CO_3 and $CaCl_2$.

The specific gravity is always < 1 The highest members, (over C_{16}), can only be distilled undecomposed in a vacuum; at the ordinary pressure they break up into olefine and water.

MONATOMIC SATURATED ALCOHOLS, $C_nH_{2n+1}OH$.

		Possible.	Known.	M. Pt.	B. Pt.
Methyl alcohol .	CH_3OH	1	1		66°
Ethyl alcohol .	C_2H_5OH	1	1	−130°	78°
Propyl alcohols .	C_3H_7OH	2	2		
1. Normal propyl alcohol . .	C—C—C*				97°
2. Isopropyl alcohol . .	(C, C)>C*				83°
Butyl alcohols .	C_4H_9OH	4	4		
1. Normal primary B. alcohol .	C—C—C—C*				117°
2. Isobutyl alcohol . .	(C, C)>C—C*				108°
3. Methyl-ethyl-carbinol .	(C—C, C)>C*				99°
4. Tri-methyl carbinol . .	(C, C, C)>C*			+25°	83°
Amyl alcohols .	$C_5H_{11}OH$	8	8		
1. Normal A. ,,	C—C—C—C—C*				137°
2. Fermentation A. alcohol .	(C, C)>C—C—C*				130°
3. Methyl-propyl-carbinol .	(C—C—C, C)>C*				118°
etc.					

		M. Pt.	B. Pt.
Hexyl alcohols	$C_6H_{13}OH$		157°
Heptyl ,,	$C_7H_{15}OH$		175°
Octyl ,,	$C_8H_{17}OH$		191°
Nonyl ,,	$C_9H_{19}OH$	−5°	213°
Decyl ,,	$C_{10}H_{21}OH$	7°	{119°†
Dodecyl ,,	$C_{12}H_{25}OH$	24°	{143°
Tetradecyl ,,	$C_{14}H_{29}OH$	38°	{167°
Hexadecyl ,, (Cetyl)	$C_{16}H_{33}OH$	49°	{189°
Octadecyl	$C_{18}H_{37}OH$	59°	{210°
Ceryl ,,	$C_{27}H_{55}OH$	79°	
Myricyl ,,	$C_{30}H_{61}OH$ or $C_{31}H_{63}OH$	85°	

The * indicates the position of the hydroxyl.

† { = under 15 m.m. pressure; the boiling points from C_6 – on are those of the normal primary alcohols.

The lowest members possess an alcoholic odour, those over C_5, an odour of fusel, and both have a burning taste, while the highest members are like paraffin in appearance and without either taste or smell.

Constitution and Isomers; Classification of the Alcohols.

From C_3H_8O on, many of the alcohols are known in different isomeric modifications, thus there are two propyl, four butyl, and seven amyl alcohols, etc.

Of these, some only are oxidizable to acids, $C_nH_{2n}O_2$, containing an equal number of carbon atoms, an aldehyde, $C_nH_{2n}O$, being formed as intermediate product. Such alcohols are termed **primary** alcohols, (primary propyl-, butyl-, and isobutyl alcohols, etc).

Another class of alcohols is not oxidizable to acids with an equal number of atoms of carbon, but to ketones, $C_nH_{2n}O$, with separation of two atoms of hydrogen, *e.g.* isopropyl alcohol yields acetone, C_3H_6O. These are termed **secondary**, (secondary butyl alcohol). Upon further oxidation the ketones do indeed yield acids which, however, contain not an equal but always a lesser number of carbon atoms, the carbon chain having thus been broken up.

Lastly, the third class of alcohols, the **tertiary**, yield upon oxidation neither aldehydes, ketones nor acids with an *equal* number of carbon atoms, but only ketones or acids containing fewer atoms of carbon.

Constitution of the Alcohols.—In the monatomic alcohols one of the hydrogen atoms plays a part different to that of the others; thus it is replaceable by metals, (K and Na), and by acid radicles, and, together with the oxygen atom, combines with the hydrogen of a halogen hydride to form water, while the other hydrogen atoms of the alcohol remain unchanged. This hydrogen atom, which has already been formulated under the Theory of Types apart from the others, is called the "typical" or "extra-radicle" hydrogen atom. It is not joined directly to the carbon atom but

through the oxygen one, which is apparent from the fact of the alcohols being capable of preparation from the monohaloid substitution products of the saturated hydrocarbons. (See p. 85.) This has been already gone into in some detail for ethyl alcohol (p. 18).

The alcohols therefore contain a hydroxyl, OH, and their general constitutional formula is $(C_nH_{2n+1}).OH$.

According to theory, this hydroxyl can either replace an atom of hydrogen in a methyl group, in which case an alcohol containing the group CH_2OH, (one carbon atom being joined to the other by a single bond), results, *e.g.* CH_3-CH_2OH. Or it can replace the hydrogen of a $CH_2=$ group in a hydrocarbon, so that the resulting compound contains the atomic group $=CH.OH$, the carbon atom being here joined to two other ones. Or, lastly, it is possible that in a hydrocarbon with branching carbon chain, the hydrogen of a methine group $CH\equiv$ (p. 30) may be replaced by hydroxyl, when the resulting compound consequently contains the group $\equiv C.OH$, in which one carbon atom is joined to other three.

Now, it is easy to see that the group $-C\begin{smallmatrix}H_2\\O.H\end{smallmatrix}$ can, by further oxidation, be transformed into this other, $-C\begin{smallmatrix}O\\O.H.\end{smallmatrix}$ The latter, which is termed carboxyl, is contained in the acids $C_nH_{2n}O_2, = C_{n-1}H_{2n-1}COOH$, which result from the oxidation of the primary alcohols. Consequently it is the **primary** alcohols which contain the atomic group $-CH_2.OH$.

The group $=CH.OH$ can likewise be changed into $=C=O$, $\left(i.e.\ C\begin{smallmatrix}OH\\OH\end{smallmatrix} - H_2O\right)$, which is the characteristic atomic group of the ketones, by oxidation. A further introduction of O or OH, whereby acids containing the group $-CO.OH$ would ensue, is not possible in this case without a rupture of the carbon chain, since carbon is tetravalent. Since then it is the **secondary** alcohols which upon oxidation yield ketones, and not acids with an equal number of carbon atoms, the group $=CH.OH$ is characteristic of these.

Finally, the atomic group $\equiv$C.OH already contains the maximum of oxygen which can be combined with a carbon atom already linked to three other atoms of carbon. A compound, therefore, in which this atomic group is present, cannot yield upon oxidation an aldehyde, acid, or ketone with an equal number of carbon atoms in the molecule, but the result of such oxidation must be the breaking of the carbon chain, and the formation of acids or ketones containing a lesser number of carbon atoms in the molecule. This being the behaviour of **tertiary** alcohols, the group $\equiv$C.OH is peculiar to them.

The existence of the three classes of alcohols finds in this way a thoroughly satisfactory explanation from theory.

The secondary and tertiary alcohols were predicted by *Kolbe* in 1859 from theoretical considerations (A. **113**, 301; **132**, 102).

Among the isomeric alcohols the primary possess the highest, and the tertiary the lowest boiling points, and the same holds good for their ethers. The tertiary have the highest melting points.

Occurrence.—Different alcohols are found in nature combined with organic acids as ethers in ethereal oils and waxes; *e.g.* methyl-, ethyl-, butyl-, hexyl-, and octyl-alcohols, and also those with 16, 27, and 30 carbon atoms; ethyl alcohol also occurs in the free state.

I. General Methods of Formation.—1. By "saponification" or "hydrolysis" of their ethers, by boiling these with alkalies or acids, or by the action of superheated steam, thus:

$$\underbrace{CH_3.O.C_7H_5O_2}_{\text{Salicylic methyl ether.}} + KOH = CH_3OH + \underbrace{C_7H_5O_2.OK}_{\text{Potassium salicylate.}}$$

Some ethers, *e.g.* ethyl-sulphuric acid, decompose when simply warmed with water:

$$C_2H_5.O.SO_3H + H_2O = C_2H_5.OH + SO_4H_2.$$

2. From the halogen compounds $C_nH_{2n+1}X$, and therefore indirectly from the paraffins and olefines (pages 68 and 70), in which latter case secondary or tertiary alcohols, from C_3 on, are obtained; this follows from the halogen of the olefine haloid compounds being linked to that carbon atom to which the fewest hydrogen atoms are attached.

a. By warming these, especially the iodides, with excess of

water to 100°; sometimes by simply allowing the mixture to stand, (tertiary iodides):

$$C_2H_5I + HOH = C_2H_5.OH + HI.$$

When but little water is used, a state of equilibrium is reached (p. 71). These halogen compounds may also be termed the halogen-hydride ethers of the alcohols, so that, strictly speaking, the mode of formation 2 is included in 1.

b. Frequently by digesting with moist silver oxide, (which acts here like the unknown hydroxide, AgOH), or by boiling with lead oxide and water:

$$C_2H_5I + Ag.OH = C_2H_5.OH + AgI.$$

c. Upon warming with silver or potassium acetate, the acetic ether of the alcohol in question is formed, and this is then saponified, thus:

$$C_2H_5I + AgO.(C_2H_3O) = C_2H_5.O.C_2H_3O + AgI.$$
$$C_2H_5O.C_2H_3O + HOK = C_2H_5.OH + (C_2H_3O)OK.$$

3. From the paraffins and olefines, by first converting these into the halogen-compounds $C_nH_{2n+1}X$ (see 2).

Since the halogen-compounds obtained from the olefines contain the halogen linked to that carbon atom to which the smallest number of hydrogen atoms are joined (see p. 71), the alcohols prepared from these are—from C_3 onwards—secondary or tertiary.

4. By the fermentation of the carbohydrates (*e.g.* grape sugar), the alcohols with 2, 3, 4, 5 and, under certain conditions, even 6 atoms of carbon are produced. (Yeast fermentation.)

4*a.* From glycerine (also from carbohydrates) by the schizomycetes fermentation, alcohols with 2, 3 and 4 carbon atoms are formed (*Fitz*).

5. On treating the primary amines with nitrous acid,* the nitrous ethers of the alcohols are got:

$$C_2H_5NH_2 + HONO = C_2H_5.OH + N_2 + H_2O.$$

6. From polyatomic alcohols by the partial action of halogen hydride and the backward substitution of the resulting compounds, *e.g.*:

$$\underbrace{C_3H_5'''(OH)_3}_{\text{Glycerine.}} + 2HCl = \underbrace{C_3H_5(OH)Cl_2}_{\text{Di-chlorhydrin.}} + 2H_2O.$$

$$C_3H_5(OH)Cl_2 + 2H_2 = \underbrace{C_3H_7OH}_{\text{Isopropyl alcohol.}} + 2HCl.$$

II. Special Methods of Formation.—1. Primary alcohols are obtained from aldehydes by reduction with sodium amalgam

* For the sake of convenience, the formula of the hypothetical nitrous acid, $NO_2H = NO.OH$, is used instead of $N_2O_3 + H_2O$.

and very dilute sulphuric acid, (*Wurtz*); or with acetic acid and zinc dust, the acetic ethers of the alcohols resulting here: $C_2H_4O + H_2 = C_2H_6O$.

Similarly from acid anhydrides and nascent hydrogen, or from a mixture of anhydride and acid chloride (see these), when the acid ether of the alcohol is formed.

In certain cases (see gluconic acid) acids can be directly reduced to alcohols by sodium amalgam (*E. Fischer*).

Since the acids can be synthetically prepared from alcohols containing one atom of carbon less than themselves, a means is thus given for converting one alcohol into another higher in series (*Lieben* and *Rossi*).

2. Secondary alcohols are formed by the action of nascent hydrogen (sodium amalgam) on the ketones, $C_nH_{2n}O$:

$$\underset{\text{Acetone.}}{CH_3—CO—CH_3} + H_2 = \underset{\text{Isopropyl alcohol.}}{CH_3—CH.(OH)—CH_3}.$$

Pinacones are obtained here as bye-products. (See Ketones.)

3. Secondary alcohols are further produced by the action of aldehydes upon zinc-methyl or zinc-ethyl.

3*a*. Also by the action of zinc-alkyl upon ethyl formate.

4. Tertiary alcohols are formed by the prolonged action of zinc-methyl or -ethyl (2 mols.) upon acid chlorides in the cold, and decomposition of the resulting product with water, (*Butlerow*). When the action is only a short one, ketones and not alcohols are got.

5. Secondary or tertiary alcohols sometimes ensue by the direct combination of an olefine with water, *e.g.* tertiary butyl alcohol, $(CH_3)_3C.OH$, from isobutylene.

The *Nomenclature* of the alcohols, especially of the secondary and tertiary, is based upon a comparison of them with methyl alcohol, also called carbinol. They are looked upon as carbinol, $CH_3.OH$, in which the three hydrogen atoms are wholly or partially replaced by alcohol radicles, thus:

tertiary butyl alcohol, $(CH_3)_3C.OH$, = tri-methyl carbinol;
secondary butyl alcohol, $CH_3—CH_2—CH(OH)—CH_3$,
= $CH(OH)(CH_3)(C_2H_5)$, = methyl-ethyl carbinol.

The "official name" of the alcohols terminates in "ol."

Behaviour of the alcohols. 1. The typical hydrogen atom (p. 82) is replaceable by metals, *e.g.* directly by K or Na, with formation of compounds termed alcoholates:

$$2C_2H_5OH + Na_2 = \underbrace{2C_2H_5ONa} + H_2.$$

These decompose again into alcohol and alkali on addition of water. (See p. 92.)

Primary and secondary, but not tertiary, alcohols combine with baryta and lime to alcoholates at 130°. Crystalline compounds are formed with calcium chloride, so that this salt cannot be used for drying the alcohols; these compounds are decomposed by water.

2. They enter into the composition of many compounds, as "alcohol of crystallization." (See pp. 88 and 92.)

3. They yield ethers with acids:

$$C_2H_5OH + \underbrace{(C_2H_3O)OH}_{\text{Acetic acid.}} = \underbrace{C_2H_5.O.(C_2H_3O)}_{\text{Ethyl acetate.}} + H_2O.$$

Of those, the benzoic ethers are specially suitable for the separation and recognition of alcohols.

4. Dehydrating agents convert them into olefines.

5. With halogen hydride or halogen phosphorus, mono-substitution products of the hydrocarbons are produced. (See p. 71.)

6. For the behaviour of primary, secondary, and tertiary alcohols upon oxidation, see p. 83 *et seq.*

The oxidation of methyl alcohol yields mostly carbonic instead of formic acid, on account of the easy oxidizability of the latter.

6*a*. The higher primary alcohols pass into the corresponding acids upon heating with soda-lime.

7. Halogens do not substitute but oxidize. (See above.)

Certain haloid ethers of polyatomic alcohols may also be regarded as substituted monatomic alcohols, *e.g.* ethylene chlorhydrin (= Monochlorethyl alcohol), $CH_2Cl—CH_2OH$, etc.

8. The primary, secondary and tertiary alcohols can also be distinguished from one another by the behaviour of their nitro-compounds, which are formed by the action of silver nitrate on the iodides (*V. Meyer*). They vary also in the rate of rapidity with which etherification begins, and the point at which it ends, *e.g.* with acetic acid.

Methyl alcohol,* *Wood Spirit*, CH_3OH. Was discovered in wood tar by *Boyle* in 1661, and its difference from ordinary alcohol recognized in 1812 by *Phillips Taylor*. Its composition was established in 1834 by *Dumas* and *Péligot*. Name derived from μέθυ, wine, and ὕλη, wood.

Occurrence. As salicylic ether in *Gaultheria procumbens* (oil of winter green, Canada); as butyric ether in the unripe seeds of Heracleum giganteum.

* "O.N." Methanol.

Formation. 1. By chlorinating methane, CH_4, and saponifying the resulting methyl chloride, (*Berthelot*).

2. From methyl iodide and water.

3. By the destructive distillation of wood.

By this distillation there are obtained—(*a*) Gases (CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_4H_8, CO, CO_2, H_2, etc.). (*b*) An aqueous distillate of "pyroligneous acid," containing methyl alcohol, acetic acid, acetone, methyl acetate, allyl alcohol, etc. (*c*) Wood-tar, containing paraffins, naphthalene, phenol, guaiacols, etc. (*d*) Wood charcoal.

4. Also by the dry distillation of vinasse.

It is prepared in quantity from the crude pyroligneous acid by repeated distillation after neutralization, and is purified by formation of the $CaCl_2$ compound, which is stable at 100°, or, better, by transformation into the oxalic or benzoic ether, both of which are easy to purify and saponify.

Properties. Colourless liquid. B. Pt. 66°. Sp. Gr. about 0·8. The alcohol of commerce usually contains acetone. Burns with a non-luminous flame. Dissolves fats, oils, etc. Acts as an intoxicant like ethyl alcohol and, like the latter, enters into the composition of compounds as "alcohol of crystallization," *e.g.* $BaO + 2CH_4O$; $MgCl_2 + 6CH_4O$; $CaCl_2 + 4CH_4O$ (six-sided plates). Is easily oxidized to formic aldehyde and formic acid, being also converted into the latter upon heating with soda-lime. Forms with metallic potassium the crystalline compound $CH_3OK + CH_3OH$. Potassium methylate, CH_3OK, is a white crystalline powder.

The anhydrous alcohol dissolves a small amount of dehydrated cupric sulphate to a blue-green solution. Distilled over heated zinc dust, it decomposes almost quantitatively into $CO + 2H_2$.

Uses.—For tar colours—(also as CH_3I and CH_3Cl); as methyl ether in the manufacture of ice; for polishes and varnishes; as *Wiggersheim's* preservative liquid; for methylating spirits of wine, etc.

Ethyl alcohol,* *Spirits of Wine*, C_2H_5OH. Liquids containing spirits of wine have been known from very early times, and their concentration either by distillation or by dehydration with carbonate of potash is also an old art. We read of it as "alcohol" in the 16th century. *Lavoisier* arrived at the qualitative, and *de Saussure* in 1808 the quantitative composition of alcohol.

* "O.N." Ethanol.

Occurrence. In the vegetable kingdom alcohol is only found occasionally, as butyric ether, but in the animal kingdom it occurs in various forms, *e.g.* in diabetic urine. It is also present in small quantity in coal tar, bone oil, wood spirit and bread, fresh English bread containing 0·3 per cent.

Formation. 1. From C_2H_6 by conversion into C_2H_5Cl and saponification of the latter according to modes of formation 1 and 2.

2. From C_2H_4 and concentrated H_2SO_4. (See pp. 56 and 84.) This method was discovered by *Faraday*, and corroborated in 1855 by *Berthelot*.

3. From aldehyde, C_2H_4O, by reduction. (*Wurtz*, A. 123.)

4. *Preparation by the vinous fermentation of sugar.* Directly from grape and fruit sugars, $C_6H_{12}O_6$, and indirectly from cane sugar, $C_{12}H_{22}O_{11}$, after previous hydration to 2 molecules $C_6H_{12}O_6$; also from malt sugar (directly), from starch, etc.

Fermentations are peculiar slow decomposition-processes of organic substances which go on, as a rule, with liberation of gas and evolution of heat, and which are induced by micro-organisms. The vinous fermentation of sugar, *i.e.* the fermentation which produces spirit, is caused by the varieties of the genus *saccharomyces*, the *yeast ferment*, which forms small oval microscopic cells, multiplying by germination. As plants, these require for their sustenance inorganic salts, but, as non-assimilating fungi, no carbonic acid.

In the vinous fermentation 94 to 95 per cent. of the sugar breaks up into alcohol and carbonic acid:

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$$

with 2·5 to 3·6 per cent. glycerine, $C_3H_8O_3$, and 0·4 to 0·7 per cent. succinic acid, $C_4H_6O_4$, as invariable bye-products. In addition to these, most of the higher homologues of ethyl alcohol are also formed—the so-called *fusel oil*—the latter resulting from the presence of foreign micro-organisms.

The chief constituent of fusel oil is fermentation amyl alcohol (iso-butyl-carbinol), $C_4H_{11}OH$, but it has also been proved to contain the two propyl alcohols (chiefly iso-propyl), normal-, iso-, and tertiary-butyl alcohols, normal and active amyl (methyl-ethyl) alcohols, together with higher homologues and ethers. They can be separated by means of their hydro-bromic ethers.

Conditions of fermentation. Fermentation can only go on

between the limits of 3° and 35°, the most favourable temperature being between 25° and 30°. The solution must not be too concentrated; the presence of air is not strictly necessary, but it has a favouring influence. Yeast loses its activity upon the addition of any reagents which destroy the cells, also when it is thoroughly dried, when heated to 60°, when treated with alcohol, acids and alkalies; the addition of small quantities of salicylic acid, phenol, corrosive sublimate, etc., also prevents fermentation.

The following materials are used for the preparation of alcohol or of liquids containing alcohol:

(*a*) Grape sugar, fruit sugar, *i.e.* grapes and other ripe fruits, for wine, etc.; (*b*) cane or beet sugar and molasses for brandy (see Sugar); (*c*) the starch of cereals for beer and corn brandy, and of potatoes for potato brandy. The starch is first converted into malt sugar and dextrine under the influence of diastase, or into grape sugar, potato sugar, and dextrine by boiling with dilute acids, and these sugars are then fermented.

A wine of medium strength contains 8½ to 10 per cent. alcohol, port wine 15 per cent., sherry up to 21 per cent., champagne 8 to 9 per cent., and beer an average of 2 to 6 per cent.

The different varieties of brandy or spirits obtained by "burning," *i.e.* by distilling fermented liquids, contain 30 to 40 per cent. alcohol, and cognac even over 50 per cent.

Purification of alcohol. It is difficult to separate alcohol completely from water by distillation, since their boiling points are only 22° apart from one another. Even after repeated rectification the distillates are found to contain water. The same reason applies to the difficulty of separating alcohol from its higher homologues (fusel oil). From an alcohol containing 30% of water the fusel oil can be extracted by chloroform.

On the large scale this separation is excellently effected by the use of dephlegmators and rectifiers or column apparatus, which are based upon the principle of partial volatilization and partial cooling of the vapours (*Adam* and *Berard;* improved by *Savalle, Pistorius, Coffey* and others.) In this way an alcohol containing 98 to 99 per cent. can be obtained.

Aqueous alcohol can be deprived of the greater part of its water by the addition of strongly heated carbonate of potash or anhydrous copper sulphate, or by distillation over

quick lime, and the last portions can be extracted by baryta, or by several additions of metallic sodium and repeated distillation. Alcohol containing water becomes turbid on being mixed with benzene, carbon bisulphide, or liquid paraffin oil, and it gives a white precipitate of $Ba(OH)_2$ on the addition of a solution of BaO in absolute alcohol. Alcohol free from water is termed *absolute* alcohol.

Contraction takes place on mixing alcohol and water together, 53·9 volumes alcohol + 49·8 volumes water giving, not 103·7, but 100 volumes of the mixture. The percentage of alcohol in any spirit is determined either from its specific gravity by reference to a specially calculated table, or by areometers of particular construction, or by its vapour tension as estimated by *Geissler's* vaporimeter.

Properties. Colourless mobile liquid with characteristic spirituous but not fusel smell. B. Pt. 78·3°, or 13° under 21 *m.m.* mercury pressure. Solidifies at $-130·5°$. Sp. Gr. 0·79 at 15°. Burns with an almost non-luminous flame. Is exceedingly hygroscopic, and miscible with water and with ether in all proportions. Forms several cryo-hydrates with water ($+12$Aq., $+3$Aq., $+\frac{1}{3}$Aq.). Is an excellent solvent for many organic substances such as resins and oils, and also dissolves sulphur, phosphorus, etc., to some extent; consequently it is much used in the laboratory. Gives with conc. H_2SO_4, according to the conditions, ethyl-sulphuric acid, ether, or ethylene. For its behaviour with HCl, etc., see p. 71. It diffuses through porous membranes into a dry atmosphere more slowly than water, and coagulates albumen, being therefore used for preserving anatomical preparations.

It is very easily oxidized by the oxygen of the air, first to aldehyde and then to acetic acid, either in presence of finely-divided platinum or in dilute solutions containing nitrogenous matters; thus, beer and wine become sour, but not the pure alcohol itself. $K_2Cr_2O_7$ or $MnO_2 + H_2SO_4$ oxidize it in the first instance to aldehyde; fuming nitric acid attacks it violently with formation of nitrogen tri- and tetr-oxides, aldehyde, ethyl nitrite, and formic, oxalic and hydrocyanic

acids, but, by the action of colourless concentrated HNO_3, ethyl nitrate can, without oxidation, be obtained; in dilute solution glycollic acid is formed. Alkalies also induce a gradual oxidation in the air; thus, alcoholic potash or soda solutions quickly become brown with formation of aldehyde resin, this latter resulting from the action of the alkali upon the aldehyde first produced. Alcoholic potash therefore frequently acts as a reducing agent, *e.g.* upon aromatic nitro-compounds. (See these.) Chlorine and bromine first oxidize alcohol to aldehyde and then act as substituents. (See Chloral.) Chlorinated alcohols can therefore only be prepared indirectly (cf. Ethylene chlorhydrin). When the vapour of alcohol is led through a red-hot tube, H, CH_4, C_2H_4, C_2H_2, C_2H_6, $C_{10}H_8$, CO, C_2H_4O, $C_2H_4O_2$, etc., are formed.

Of the compounds containing alcohol of crystallization may be mentioned, $KOH + 2C_2H_6O$, $LiCl + 4C_2H_6O$, $CaCl_2 + 4C_2H_6O$, and $MgCl_2 + 6C_2H_6O$.

Sodium Ethylate, C_2H_5ONa, is of special importance among the alcoholates. It is formed by the action of sodium upon absolute alcohol. The crystals of $C_2H_5.ONa + 2C_2H_6O$, at first obtained, lose their alcohol of crystallization at 200° and change into a white powder of C_2H_5ONa. Sodium ethylate is of especial value for syntheses, and can frequently be employed in alcoholic solution.

When taken in small quantity alcohol acts as a stimulant and an aid to digestion, in larger quantity as an intoxicant. Absolute alcohol is poisonous, and quickly causes death when injected into the veins.

Detection of alcohol. 1. By the iodoform reaction (see Iodoform), when 1 part in 2,000 of water can be recognized.

2. By means of benzoyl chloride, C_6H_5COCl, which yields with alcohol the characteristically-smelling benzoic ethyl ether.

Propyl alcohols, C_3H_7OH.

1. Normal propyl alcohol,* *ethyl carbinol*, $CH_3—CH_2—CH_2OH$, (*Chancel*, 1853), is obtained from fusel oil by means of its hydrobromic ether (*Fittig*), or directly by fractionation. It has also been got from propionic aldehyde and propionic anhydride by reduction with sodium amalgam (*Rossi*). It is a liquid with a

pleasant spirituous odour, and boils 19° higher than ethyl alcohol. Miscible with water in every proportion, and again separated out on addition of chloride of calcium. Gives propionic acid upon oxidation. Its *constitution* follows from that of propionic acid, and from the preparation of the latter from ethyl alcohol.

2. Secondary propyl alcohol,* *isopropyl alcohol, or dimethyl carbinol*, $(CH_3)_2{=}CH.OH$, (*Berthelot*, 1855), was at first held to be primary. It is obtained from isopropyl iodide (from glycerine) by methods I. 2*a* and 2*b*, also by the action of sodium amalgam on acetone by method II. 2, (*Friedel*, 1862). It also results unexpectedly, instead of the normal alcohol, from normal propylamine by method I. 4, on account of the intermediate formation of C_3H_6. Colourless liquid. Boils about 15° lower than its isomer, and like it can be "salted out" from aqueous solution. Gives acetone upon oxidation. The *constitution* of isopropyl alcohol follows from its formation from acetone, whose constitution is $CH_3{-}CO{-}CH_3$.

Butyl alcohols, C_4H_9OH. The four isomers which are theoretically possible are known.

1. **Normal butyl alcohol,**† $CH_3{-}CH_2{-}CH_2{-}CH_2OH$. Present in fusel oil, being formed especially in the wine-yeast fermentation (by elliptical yeast). Is got rather easily from glycerine by the schizomycetes fermentation, (*Fitz*). Prepared from butyl aldehyde, butyric acid or butyryl chloride, according to II. 1 (*Lieben* and *Rossi*, 1869). Boils 19° higher than normal propyl alcohol. Has a peculiar odour, and gives rise to coughing when inhaled. Is not miscible with water in all proportions, 1 volume requiring 12 volumes water for solution at the ordinary temperature. Can be "salted out" from its solution. Gives normal butyric acid, $C_4H_8O_2$, on oxidation. Its *constitution* follows from its relation to the acid (see this), and from the preparation of the acid from normal propyl alcohol.

2. **Secondary butyl alcohol,**‡ *methyl-ethyl-carbinol*, or *butylene hydrate*, $\begin{matrix}C_2H_5\\CH_3\end{matrix}{>}CHOH$, $= CH_3{-}CH_2{-}CH(OH){-}CH_3$. The hydriodic ether is formed from erythrite, $C_4H_6(OH)_4$, and HI (*de Luynes*), or from

normal butylene and HI, and is then saponified according to I. 2. The alcohol is also obtained from aldehyde and zinc ethyl, according to II. 3, and from formic ether according to II. 4, (*Saytzeff*). Strongly smelling liquid, boiling about 18° lower than the normal alcohol. Gives methyl-ethyl ketone upon oxidation, from which its *constitution* follows.

3. **Isobutyl alcohol,*** or *fermentation butyl alcohol,*

$$(CH_3)_2=CH-CH_2OH,$$

is the most important of the butyl alcohols. It is contained in fusel oil, (*Wurtz*, 1852), especially in potato fusel oil—(beer-yeast fermentation)—, and is best isolated from this as the iodide. Colourless liquid, with a spirituous fusel smell resembling that of wild jasmine. Boils about 8° lower than the normal alcohol. Yields isobutyric acid, $C_4H_8O_2$, on oxidation, hence its *constitution.*

4. **Trimethyl carbinol,**† or *tertiary butyl alcohol,* $(CH_3)_3\equiv C.OH$, (*Butlerow*, 1863). Is contained in small quantity in fusel oil. Prepared, *e.g.* according to II. 5, but more simply by the action of 75 per cent. H_2SO_4 on isobutylene, from isobutyl alcohol. (See II. 5.) Rhombic prisms or tables. Smell spirituous and resembling that of camphor. M. Pt. 23·5°; B. Pt. 33° below that of the normal alcohol. Yields acetone, acetic acid and carbonic acid on oxidation. Its *constitution* follows, for instance, from method of formation II. 5, and also from the constitution of tertiary butyl iodide (pp. 51 and 75).

Amyl alcohols, $C_5H_{11}OH$. Theoretically eight isomers are possible, four primary, three secondary and one tertiary, and all of these are known.

1. **Normal primary amyl alcohol** (1-*Pentanol*).

$$CH_3-CH_2-CH_2-CH_2-CH_2.OH,$$

is contained in small quantity in fusel oil, and can be prepared from normal valeric aldehyde, (*Lieben* and *Rossi*), and from normal pentane, by formation of $C_5H_{11}Cl$.

2. **Isobutyl carbinol,**‡ $(CH_3)_2=CH-CH_2-CH_2OH$, (*Erlenmeyer*), forms the chief constituent of "fermentation amyl alcohol," which was already known to *Scheele*, and is also found in nature in Roman camomile oil. It was prepared synthetically from isobutyl alcohol in 1876 by the *Lieben-Rossi* method. M. Pt. −134°; B. Pt. 131°. Has a fusel smell and burning taste, and is poisonous; causes the disagreeable toxic after-effects of intoxication by brandy, etc.

* 2-Methyl-3-Propanol. † 2-Methyl-2-Propanol. ‡ 2-Methyl-4-Butanol.

3. **Secondary Butyl-carbinol**,* *active amyl alcohol*, $\frac{CH_3}{C_2H_5}>CH-CH_2OH$ (*Pasteur*, 1855), is also contained in fermentation amyl alcohol. It turns the plane of polarization of light to the left, its chloride, bromide, iodide, and the valeric acid resulting from its oxidation being also optically active (dextro-rotatory).

The action upon polarized light is connected with the presence of an "asymmetric" carbon atom. (See p. 40.) A dextro-rotatory modification of this alcohol, obtained from it by fission-fungus fermentation (p. 39) exists, its iodide being laevo-rotatory.

Amylene hydrate (*2-Methyl-2-Butanol*), *tertiary amyl alcohol*, $\frac{CH_3}{CH_3}>C(OH)-CH_2-CH_3$, results from the indirect union of amylene with water. It acts as a hypnotic.

Hexyl alcohols, *Caproyl alcohols*, $C_6H_{13}.OH$. Of these seventeen are possible, and eleven are already known.

Normal primary hexyl alcohol, obtained from normal hexane and also from caproic acid, $C_6H_{12}O_2$, is found in nature as butyric ether, *e.g.* in the essential oil of Heracleum sphondylium. Isomeric with it is primary fermentation hexyl alcohol from wine fusel oil.

Heptyl alcohols, (*Oenanthyl alcohol*), $C_7H_{15}OH$. Thirty-eight are possible, and, up to now, thirteen or fourteen are known.

Octyl alcohols, $C_8H_{17}OH$. The normal octyl alcohol is found as acetic ether, together with hexyl alcohol, in varieties of *Heracleum*, etc.

Normal Decyl alcohol, $C_{10}H_{21}OH$, **Dodecyl alcohol**, $C_{12}H_{25}OH$, **Tetradecyl alcohol**, $C_{14}H_{29}OH$, **Hexadecyl alcohol**, $C_{16}H_{33}OH$, and **Octadecyl alcohol**, $C_{18}H_{37}OH$, were prepared by *Krafft* in 1881, by reducing the corresponding acids with zinc dust and acetic acid. They are solid and like paraffin in appearance.

Normal Hexa-decyl-alcohol, also called **Cetyl alcohol**, or *Ethal*, forms as palmitic ether the chief constituent of spermaceti. The cetyl alcohol of commerce contains, besides, a homologous alcohol, $C_{18}H_{38}O$.

Ceryl alcohol, *cerotin*, $C_{27}H_{55}OH$, forms as cerotic ether Chinese wax.

Melissic or **Miricyl alcohol**, $C_{30}H_{61}OH$ or $C_{31}H_{63}OH$, is present as palmitic ether in bees' wax and in Carnauba wax, and is most conveniently prepared from the latter. The alcohols are obtained from all these ethers (wax varieties) by saponification with boiling alcoholic potash.

B. Monatomic Unsaturated Alcohols, $C_nH_{2n-1}OH$.

These are very similar to the saturated alcohols both in physical properties and in general chemical behaviour, but are sharply distinguished from the latter by their capability of taking up 2 atoms of halogen or of hydrogen, or 1 molecule of

* 2-Methyl-1-Butanol.

halogen hydride, and thereby forming saturated alcohols or their mono- or di-haloid substitution products. (These latter, as already mentioned at p. 87, cannot be prepared by direct substitution of the alcohols.) They thus behave in this respect like the olefines, C_nH_{2n}, and so the existence of a double carbon bond must be assumed in their case also. They are to be considered as olefines in which an atom of hydrogen is replaced by hydroxyl.

From $C_3H_5.OH$ onwards, they yield triatomic alcohols upon careful oxidation (B. **21**, 3347).

According to theory, the existence of alcohols which contain the oxymethylene group, CH(OH), linked to a carbon atom by a double bond, might be predicted. To this class belongs **Vinyl alcohol** (*Ethenol*), $CH_2=(CH—OH)$, which occurs in commercial ether, but which has not yet been isolated (B. **22**, 2863), although derivatives of it are known. By the reactions in which one would expect it to be formed, its isomer aldehyde, $CH_3.CHO$, results; in fact, the atomic group $=C=CH.OH$ is for the most part unstable, passing as it does into the more stable one $=CH—CHO$, which is explicable upon the assumption that water, H.OH, is taken up and again split off. Similarly, instead of the group $CH_2=(COH)—CH_3$, we always get the other, $CH_3—CO—CH_3$.

Allyl alcohol (*Propenol*), $C_3H_5.OH$, = $CH_2=CH—CH_2OH$ (*Cahours* and *Hofmann*, 1856). Present to the extent of 0·1 to 0·2 per cent. in wood spirit. Is formed (1) from allyl iodide; (2) by reduction of its aldehyde, acrolein (see this); (3) by heating glycerine, $C_3H_5(OH)_3$, with oxalic or formic acid and some ammonium chloride to 260°. This last reaction appears to be a reduction process, thus, $C_3H_8O_3 - H_2O - O = C_3H_6O$; as intermediate product, however, a formic ether of glycerine (see monoformin) is obtained. Allyl alcohol is a mobile liquid of suffocating smell, having almost the same boiling point (97°) as N-propyl alcohol; like the latter it is miscible with water. It does not take up nascent hydrogen directly, but chlorine, bromine, cyanogen, hypochlorous acid, etc. If cautiously oxidized, it yields glycerine, but stronger oxidation converts it into its aldehyde, acrolein, and acid, acrylic acid, containing the same number of carbon atoms, and it is therefore a primary alcohol; hence the above *constitutional formula*.

Monobromo-allyl alcohol, $CH_2=CBr—CH_2.OH$, results from tribromhydrin, by successive treatment with potash and carbonate of potash. Liquid; B. Pt. 155°.

Several higher homologues are known.

C. Monatomic Unsaturated Alcohols, $C_nH_{2n-3}.OH$.

These alcohols are derivatives of acetylene and its homologues. In addition therefore to the general properties of the alcohols, and those common to the unsaturated alcohols of combining directly with 4 atoms of H, Cl, Br, or 2 molecules HCl, HBr, etc., most of them possess the further peculiarity of forming explosive compounds with ammoniacal copper and silver solutions, *e.g.* C_3H_2AgOH, the former being coloured, *e.g.* yellow, and the latter white; acids decompose these compounds backwards again. Those of them which do not yield such metallic compounds contain, not a triple bond, but two double ones between the carbon atoms. The most important of the alcohols is

Propargyl alcohol, or *propinyl alcohol* (*Propinol*),

$$C_3H_3OH, = CH \equiv C—CH_2OH,$$

a mobile liquid of agreeable odour, lighter than water, and boiling at 114°, *i.e.* somewhat higher than normal propyl alcohol.

It is prepared by treating monobrom-allyl alcohol with potash; can take up 4 atoms of bromine.

IV. DERIVATIVES OF THE ALCOHOLS.

These may be classed in the following divisions:—

1. Ethers of the alcohols, *e.g.* $C_2H_5.O.C_2H_5$, ethyl ether.
2. Thio-alcohols and ethers, *e.g.* $C_2H_5.SH$.
3. Compound ethers and acid derivatives of the alcohols.
4. Nitrogen bases of the alcohol radicles.
5. Other metalloid compounds of the alcohol radicles.
6. Metallic compounds of the alcohol radicles, or organometallic compounds.

A. Ethers Proper, (Alcoholic Ethers).

Under ethers of the monatomic alcohols are understood compounds of neutral character derived from the alcohols by elimination of the elements of water, (1 molecule water from 2 molecules alcohol). They can frequently be prepared by treating the alcohols with sulphuric acid, and are distinguished

from the latter by not combining with acids to form ethers, and by being substituted and not oxidized by the halogens, etc. Only the lowest member of the series is gaseous, most of them are liquid, and the highest are solid. The more volatile ethers are characterized by a peculiar odour which vanishes as the series ascends.

Unlike the alcohols, no one hydrogen atom in the ethers plays a part different to that of the others; consequently metallic sodium has no action upon them. (See p. 18.)

Constitution. The ethers may be regarded as the anhydrides of the monatomic alcohols, analogous to the anhydrides of the mono-acid bases:

$$\begin{matrix} K\,OH \\ KO\,H \end{matrix} = K_2O + H_2O; \quad \begin{matrix} C_2H_5\,OH \\ C_2H_5O\,H \end{matrix} = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!>\!O + H_2O.$$

For their re-transformation into alcohols, see below.

They may also be considered as the oxides of the alcohol radicles, *e.g.* $(C_2H_5)_2O$, ethyl ether; or, lastly, as alcohols in which the typical hydrogen atom is replaced by an alcoholic radicle:

$C_2H_5.OH$	$C_2H_5.O(C_2H_5)$	$C_2H_5.O(CH_3)$
Alcohol.	Ether.	Ethyl-methyl ether.

The alcoholic radicles contained in them may either be the same, as in ordinary ether and in methyl ether, $(CH_3)_2O$, in which case they are termed "**simple ethers**"; or they may be different, as in methyl-ethyl ether, when they are known as "**mixed**" or "**intermediate ethers.**" The compound ethers of the acids are also frequently termed "ethers," *e.g.* "acetic ether" = ethyl acetate; also frequently "esters."

Ethers of tertiary alcohols are not known.

Modes of formation. 1. By heating the alcohols, $C_nH_{2n+1}.OH$, with sulphuric acid. The reaction goes on in two phases, *e.g.* for ethyl ether thus:

a. $C_2H_5OH + SO_4H.H = C_2H_5.(SO_4H) + H_2O.$

b. $C_2H_5SO_4H + C_2H_5.OH = C_2H_5.O.C_2H_5 + H_2SO_4.$

In phase *a* an ether-sulphuric acid is formed, which, when further heated with alcohol, as in *b*, yields ether and regenerates sulphuric acid. The latter is therefore free to work anew,

and in this way to convert a very large quantity of alcohol into ether.

This process is theoretically a continuous one, but practically it has its limits, through secondary reactions, such as the formation of SO_2, etc. The method is only suitable for primary alcohols, secondary and tertiary going too easily into olefines. Hydrochloric, hydrobromic and hydriodic, among other acids, act similarly to sulphuric acid; thus ether is obtained upon heating alcohol with dilute hydrochloric acid in a sealed tube to 180°, ethyl chloride, C_2H_5Cl, being formed as intermediate product, and then reacting to yield alcohol in a way analogous to that given in the following mode of formation. Upon heating alcohol with hydrochloric acid there ensues, however, a state of equilibrium between the alcohol, ether, ethyl chloride, hydrochloric acid and water, after which the same quantity of each of these products is destroyed as is formed in unit of time.

2. By the action of halogen-alkyl upon sodium-alkylate, or also upon alcoholic potash:

$$C_2H_5I + C_2H_5.ONa = C_2H_5.O.C_2H_5 + NaI.$$

3. From halogen-alkyl and dry silver oxide, Ag_2O, (also HgO and Na_2O):

$$2C_2H_5I + Ag_2O = C_2H_5.O.C_2H_5 + 2AgI.$$

Modes of formation 1 and 2 yield mixed as well as simple ethers, *e.g.*:

$$C_2H_5.SO_4H + CH_3.OH = C_2H_5.O.CH_3 + H_2SO_4.$$

$$C_5H_{11}I + CH_3.ONa = C_5H_{11}.O.CH_3 + NaI.$$

Properties. 1. The ethers are very stable. Ammonia, alkalies, dilute acids, and metallic sodium have no action upon them, nor has phosphorus pentachloride in the cold.

2. When superheated with water in presence of some acid, such as sulphuric, the ethers take up water and are re-transformed into alcohols, the secondary more readily than the primary.

This change also goes on, but extremely slowly, simply upon standing.

3. Upon warming with concentrated sulphuric acid, alcohol and ethyl-sulphuric acid are formed:

$$C_2H_5O.C_2H_5 + HHSO_4 = C_2H_5.OH + C_2H_5.(SO_4H).$$

4. Saturated with hydriodic acid gas at 0°, the ethers split up into alcohol and alkyl iodide:

$$C_2H_5.O.C_2H_5 + HI = C_2H_5.OH + C_2H_5I.$$

When the ethers are "mixed," the iodine attaches itself to the radicle poorer in carbon; further interaction yields, of course, two molecules alkyl iodide.

5. When heated with halogen-phosphorus, the oxygen atom is replaced by two of halogen, two molecules of halogen-alkyl resulting.

6. Like the alcohols, the ethers are oxidizable, *e.g.* by nitric and chromic acids, but halogens substitute in them and do not oxidize; in this latter respect they resemble the hydrocarbons.

Ethyl ether,* "*Ether*," $(C_2H_5)_2O$.

Discovered by *Valerius Cordus* about 1544, and possibly before that time by *Raymond Lully*. It was also called "sulphuric ether," and "vitriol ether," on account of its being supposed to contain sulphur. Its composition was established by *Saussure* in 1807, and *Gay Lussac* in 1815.

Preparation. By the continuous process from ethyl alcohol and sulphuric acid at 140°, with gradual addition of the alcohol, according to *Boullay*. It is freed from alcohol by shaking with water, and dried by distillation over lime or calcium chloride, and finally over metallic sodium.

Theories of the formation of Ether. At first the action of the sulphuric acid was considered to consist in an abstraction of water. Later on, it was thought that the acid gave rise to a contact action, (*Mitscherlich*, *Berzelius*), but *Liebig* showed that this view was incorrect, since ethyl-sulphuric acid is formed. *Liebig* assumed that ethyl-sulphuric acid broke up, upon heating, into ether and SO_3, but *Graham*, on the other hand, proved that the acid gives no ether when heated alone to 140°, but only when heated along with more alcohol.

After this, *Williamson* propounded the theory of etherification at present held, a theory based on the opinion of *Laurent* and *Gerhardt* that ether contains two ethyl radicles. Its correctness was proved by mode of formation 2, and also by the preparation of mixed ethers.

Properties. Mobile liquid with powerful ethereal odour, very volatile. M. Pt. −129°; B. Pt. +34°·9; Sp. Gr. at 17°·4, 0·72. Vapour tension equal to 10 atmospheres at 120°. Produces great cold on evaporation. Is easily inflammable, and therefore dangerous as a cause of fire, from the dissemination of its very heavy vapour; a mixture of it with oxygen or air is explosive. It is somewhat soluble in water (1 part in 10), and, conversely, 3 volumes of water dissolve in 100 volumes of ether; the

* Ethane-oxy-ethane.

presence of water can be detected by the milkiness which ensues upon the addition of carbon bisulphide. Miscible with concentrated hydrochloric acid. Ether is an excellent solvent or extractive for many organic substances, and also for I, Br, CrO_3, Fe_2Cl_6, $AuCl_3$, $PtCl_4$ and other chlorides. It forms crystalline compounds with various substances, *e.g.* the chlorides and bromides of Sn, Al, P, Sb, and Ti, being present in them as "ether of crystallization."

When dropped upon platinum black it takes fire, and when poured into chlorine gas an explosion results, hydrochloric acid being set free. In the dark, however, and in the cold, substitution by chlorine is possible; the final product of the substitution, **perchloro-ether**, $C_4Cl_{10}O$, is solid and smells strongly like camphor.

Uses. Ether was first employed as an anæsthetic by *Simpson* in 1848, but this property had been previously observed by *Faraday*. It is further used as an extractive in the colour industry, as *Hoffmann's* drops when mixed with 1 to 3 volumes of alcohol, for ice machines, and for the preparation of collodion, etc.

Dichloro-ether, $C_4H_8Cl_2O$. Two isomeric forms of this are known, of which the unsymmetrical is prepared from ether and chlorine, and the symmetrical from aldehyde and hydrochloric acid. Both are liquids.

Methyl ether, $(CH_3)_2O$ (*Dumas, Péligot*), closely resembles common ether; gaseous at the ordinary temperature, but liquid under −20°. It is prepared on the large scale for the production of artificial cold.

Ethyl-cetyl- and **Di-cetyl ethers** are solid at the ordinary temperatures.

Several ethers with unsaturated alcohol radicles are also known, *e.g.* **Allyl ether,** $(C_3H_5)_2O$, and **Vinyl-ethyl ether,** $C_2H_3—O—C_2H_5$, B.Pt. 35°·5. These can combine directly with bromine.

Isomers. The general formula of the saturated ethers is $C_nH_{2n+2}O$. To each ether there is therefore a corresponding saturated alcohol which is isomeric with it, thus C_2H_6O = methyl ether or ethyl alcohol, $C_4H_{10}O$ = di-ethyl ether or butyl alcohol, and so on. From $C_4H_{10}O$ on, however, several different isomeric ethers are not only possible, but are also known, *e.g.* di-ethyl ether, $(C_2H_5)_2O$, is isomeric with methyl-propyl ether, $CH_3.O.C_3H_7$; similarly methyl-amyl ether, $CH_3.O.C_5H_{11}$,

ethyl-butyl ether, $C_2H_5.O.C_4H_9$, and di-propyl-ether, $C_3H_7.O.C_3H_7$ are all isomeric. Isomerism of this kind depends upon the fact that the alcoholic radicles—and hydrogen—are homologous, so that for equal sums total of carbon atoms the sums of the hydrogen atoms must also be equal.

Such isomerism, which depends upon the grouping together by a polyvalent element—in this case, oxygen—of alcohol radicles which are individually unequal, but the sums of whose elements taken together are equal, is called **metamerism.** One of the alcohol radicles may here be replaced by hydrogen.

The establishing of the *constitution* of the ethers is based upon (*a*) their syntheses according to modes of formation 1 or 2, and (*b*) their decomposition by HI according to p. 99.

Alcohols and ethers containing an equal number of carbon atoms are therefore metameric. Alcohols are accordingly compounds which contain hydrogen and one alcohol radicle joined together by means of oxygen. Ethers, on the other hand, are compounds containing two alcohol radicles similarly joined.

It stands to reason, of course, that all those varieties of isomerism which are found in the alcohols, and therefore in the alcohol radicles, can also occur in the ethers which contain these radicles.

Varieties of Isomerism. The cases of isomerism which have been mentioned up to now are of three kinds. The first was the isomerism of the higher paraffins, which, since it is based upon the dissimilarity of the carbon chains, is often termed chain-isomerism. The isomerism between ethylene and ethylidene chlorides or between primary and secondary propyl alcohols depends upon the differences in position of the substituting halogen or hydroxyl in the same carbon chain, and is termed isomerism of place or position. In addition to these there is the third kind, metamerism. Further cases will be spoken of under the Benzene derivatives.

B. Thio-alcohols and -ethers.

Methyl mercaptan, $CH_3.SH$, (*Dumas* and *Péligot*). B. Pt. 6°.
Ethyl mercaptan, $C_2H_5.SH$, (*Zeise*, 1833). B. Pt. 36°.
Methyl sulphide, $(CH_3)_2S$, (*Regnault*). B. Pt. 37°.
Ethyl sulphide, $(C_2H_5)_2S$. B. Pt. 92°, etc.

From the alcohols and ethers sulphur compounds are derived,

by the replacement of one atom of oxygen by one of sulphur. These are liquids of a most unpleasant and piercing odour, something like that of leeks; they are nearly insoluble in water and the lower members are very volatile. The higher homologues are not so soluble in water, but continue soluble in alcohol and ether, and their smell is less strong on account of the rise in the boiling point. They are readily inflammable.

The Thio-alcohols, also called mercaptans* or alkyl sulph-hydrates, *e.g.* mercaptan,† $C_2H_5.SH$, although of neutral reaction, possess the chemical characters of weak acids and are capable of forming salts, the "mercaptides," especially mercury compounds. The name "mercaptan" is derived from "corpus mercurio aptum." They are soluble in a strong solution of potash, and they boil at temperatures distinctly lower than the corresponding alcohols do. The Thio-ethers, also termed alkyl sulphides, *e.g.* ethyl sulphide, $(C_2H_5)_2S$, are on the other hand neutral volatile liquids without acid character.

Both classes of compounds are derived from hydrogen sulphide by the replacement of either one or both atoms of hydrogen by alcohol radicles, just as alcohol and ether are derived from water:

$$\left.\begin{matrix}H\\H\end{matrix}\right\}S. \qquad \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S. \qquad \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S.$$

If only one of the atoms in hydrogen sulphide is substituted by an alcohol radicle, the remaining atom preserves in the new compound its original character and is easily replaceable by metals. The mercaptans are therefore monatomic compounds of faintly acid character.

The above thio-compounds are not termed ethers of hydrogen sulphide because they are not saponifiable.

The *constitution* of these compounds follows at once from their modes of formation.

Formation. The mercaptans result:

1. By warming halogen alkyl or alkyl sulphate with potassium sulph-hydrate in concentrated alcoholic or aqueous solution:

$$C_2H_5Br + KSH = C_2H_5.SH + KBr.$$

* "O.N" Thiols. † Ethane-thiol.

2. By heating alcohol with phosphorus sulphide, the oxygen being thus replaced by sulphur, (*Kekulé*).

The thio-ethers are similarly obtained—

1. From halogen alkyl or alkyl sulphate and neutral potassium sulphide:

$$2C_2H_5.SO_4K + K_2S = (C_2H_5)_2S + 2K_2SO_4.$$

2. By treating ether with phosphorus pentasulphide.
3. From halogen alkyl and sodium mercaptide.
4. By the distillation of mercury mercaptide, HgS being formed at the same time.
5. In the case of certain complex compounds, especially in the aromatic group, sulphur may be directly substituted for hydrogen on heating; this cannot be done, however, with the paraffin hydrocarbons.

"Mixed sulphides," comparable with the "mixed ethers," can also be prepared, *e.g.* methyl-ethyl sulphide, $C_2H_5.S.CH_3$.

Behaviour. A. **The Mercaptans.**

Sodium and potassium act upon the mercaptans to form sodium and potassium salts, white crystalline compounds, which are decomposed by water. The mercury salts are got by warming an alcoholic solution of mercaptan with mercuric oxide, *e.g.* mercuric mercaptide, $Hg(C_2H_5S)_2$, (white plates). With mercuric chloride difficultly soluble double compounds are formed, *e.g.* $(C_2H_5.S)Hg.Cl$, a white precipitate. The lead salts are mostly yellow-coloured, and are produced upon mixing alcoholic solutions of mercaptan and lead acetate. The copper salt of mercaptan is a bright yellow precipitate.

2. Upon oxidation with nitric acid the mercaptans are transformed into alkyl-sulphonic acids, thus:

$$C_2H_5.SH + 3O = C_2H_5.SO_3H, \text{ (ethyl-sulphonic acid).}$$

3. The mercaptans in the form of sodium salts are oxidized by iodine or by sulphuryl chloride, SO_2Cl_2, (B. **18**, 3178), and also frequently in ammoniacal solution in the air to *di sulphides*, *e.g.* **ethyl di-sulphide**, $(C_2H_5)_2S_2$, thus:

$$2C_2H_5S.Na + I_2 = (C_2H_5)_2S_2 + 2NaI.$$

These are disagreeably smelling liquids, which have a much higher boiling point than the mercaptans, are again reduced by nascent hydrogen, and yield with nitric acid di-sulph-oxides, *e.g.* **ethyl di-sulph-oxide**, $(C_2H_5)_2S_2O_2$.

4. By the action of concentrated sulphuric acid disulphides result, and not compounds analogous to ethyl-sulphuric acid.

B. The Thio-ethers.

1. They yield double compounds with metallic salts, *e.g.* $(C_2H_5)_2S, HgCl_2$, which can be crystallized from ether.

2. They are capable of combining with halogen or oxygen. Thus ethyl sulphide forms with bromine a dibromide, crystallizing in yellow octohedra:

$$(C_2H_5)_2S + Br_2 = (C_2H_5)_2SBr_2;$$

and with dilute nitric acid, **di-ethyl sulph-oxide**:

$$(C_2H_5)_2S + O = (C_2H_5)_2SO$$

a thick liquid soluble in water, which combines further with nitric acid to the compound, $(C_2H_5)_2SO, HNO_3$. Concentrated nitric acid or permanganate of potash oxidizes the sulphides or sulph-oxides to sulphones, *e.g.* ethyl sulphide to (di)-ethyl sulphone, $(C_2H_5)_2SO_2$, and methyl-ethyl sulphide to methyl-ethyl sulphone, $(CH_3)(C_2H_5)SO_2$. The sulphones are solid well-characterized compounds which boil without decomposition.

The sulph-oxides are reduced by nascent hydrogen to sulphides, but not the sulphones.

3. The behaviour of the sulphides towards the halogen alkyls is of especial interest. Thus the substances $(CH_3)_2S$ and CH_3I combine even in the cold to the white crystalline **tri-methyl-sulphine iodide**, $(CH_3)_3SI$, which is soluble in water, and which goes back into its components upon heating. This compound behaves exactly like a salt of hydriodic acid, and yields with silver oxide—(but not with alkali)—an oily base, **tri-methyl-sulphine hydroxide**, $(CH_3)_3S.OH$, which cannot be volatilized without decomposition. This is as strong a base as caustic potash and resembles the latter so closely that it absorbs carbonic acid, cauterizes the skin, drives out ammonia, and gives salts with acids with the evolution of heat, etc., etc.; it also yields salts with hydrogen sulphide which are extremely like the alkaline sulphides, *e.g.* they dissolve Sb_2S_3, (*Oefele*, 1833; *Cahours*).

Methyl Sulph-hydrate (*Methane-thiol*), $CH_3.SH$ (*Dumas* and *Péligot*). This is found among the gaseous products of the fermentation of albumen,

etc., when air is excluded, and therefore (*e.g.*) in human intestinal gases; also in urine after the consumption of asparagus. It is a liquid of repulsive odour, lighter than water; B. Pt. 6°.

Methyl Sulphide (*Methane-thio-methane*), $(CH_3)_2S$ (*Regnault*). A colourless liquid of unpleasant odour; B. Pt. 37°.

Ethyl Sulph-hydrate ("O.N." *Ethane-thiol*), *Ethyl mercaptan*, "*Mercaptan*," $C_2H_5.SH$, = $CH_3—CH_2.SH$ (*Zeise*, 1833). A liquid of extremely repulsive odour; B. Pt. 36°. It yields with metallic sodium or with sodium ethylate in alcohol:—

Sodium Mercaptide, $C_2H_5.SNa$, a white crystalline mass.

Mercuric Mercaptide $(C_2H_5.S)_2Hg$ (see above), crystallizes from alcohol in colourless plates. Mercaptan yields with mercuric chloride the compound $C_2H_5—S—HgCl$, as a white precipitate.

Ethyl Sulphide, "*Di-ethyl Sulphide*," *Thio-ethyl*, $(C_2H_5)_2S$. A liquid insoluble in water; B. Pt. 92°. Its bromine compound, $(C_2H_5)_2SBr$ (see above), forms yellow octahedra.

Ethyl Disulphide (*Ethane-dithio-ethane*), $(C_2H_5)_2S_2$, is prepared by acting on mercaptan with iodine. It is an unpleasant smelling liquid of relatively high boiling point (151°).

Ethyl Sulph-oxide (*Ethane-sulphoxy-ethane*), *Diethyl sulph-oxide*, $(C_2H_5)_2SO$. This is a thick liquid which is miscible with water. It can unite with 1 mol. nitric acid; is easily reducible to the sulphide.

Ethyl Sulphone (*Ethane-sulphone-ethane*), *Diethyl sulphone*, $(C_2H_5)_2SO_2$. Crystalline; boils without decomposition, and is not reducible.

Trimethyl-sulphine iodide, $(CH_3)_3SI$ (see above), is also obtained by warming methyl iodide and sulphur together. It forms colourless crystals which are soluble in water.

Trimethyl-sulphine hydroxide, $(CH_3)_3S.OH$ (*Oefele*, 1833, *Cahours*). This is prepared by acting upon the iodide with moist oxide of silver. For its properties see preceding page.

The compounds just described are of particular interest with regard to **the question of the valency of sulphur.**

Since in ethyl sulphide both the alcohol radicles are bound to the sulphur, this will also be the case in ethyl sulphone, otherwise the sulphones would manifestly be easily saponifiable. (See Ethyl-sulphurous acid.) Probably the sulphur in them is hexavalent, corresponding

with the formula, $\frac{C_2H_5}{C_2H_5}>S\lessgtr^{O}_{O}$. Isomers of the sulphones, which are readily saponifiable, have recently been prepared (*Otto*, B. **18**, 2500). The sulphinic hydroxides also can only be explained very insufficiently as addition compounds, on the assumption of the divalence of sulphur. The formula $(CH_3)_2S + CH_3OH$ for tri-methyl-sulphine hydroxide does not indicate in the least the strongly basic character of this substance, since it is not explicable why the mere addition of the neutral methyl alcohol to the equally neutral methyl sulphide should produce such an effect. More probable is one of the two formulae—

$$(CH_3)_3\overset{IV.}{\equiv}S-(OH)\ ;\ \text{or},\ (CH_3)_3\overset{VI.}{\equiv}S-(OH)\ ;$$

even if they do not overcome all the difficulties involved.

With respect to **isomers**, the same general conditions prevail in the sulphur as in the corresponding oxygen compounds.

Sulphides of Unsaturated Alcohol Radicles.

Vinyl Sulphide,* $(C_2H_3)_2S$. Present in Allium ursinum. B. Pt. 101°.

Allyl sulphide,† $(C_3H_5)_2S$ (*Wertheim*, 1844), present in the oil of Allium sativum—oil of garlic,—in Thlapsi arvense, etc. Prepared from allyl iodide and K_2S (*Hofmann*, *Cahours*). B. Pt. 140°.

Analogous **selenium and tellurium compounds** of alcohol radicles are also known. They are in part distinguished by their excessively disagreeable, nauseous and persistent odour.

C. Ethers (Esters) of the Alcohols with Inorganic Acids and their Isomers.

The compound ethers may be considered as derived from the acids, (see pp. 79 and 87), by the exchange of the replaceable hydrogen of the latter for alcoholic radicles, just as salts result by exchanging the hydrogen for a metal—

$$HNO_3. \qquad KNO_3. \qquad (C_2H_5)NO_3.$$

Or, they are derived from the alcohols by exchange of the alcoholic hydrogen atom for an acid radicle, *i.e.* for the acid residue which is combined with OH—

$$C_2H_5.O.H. \qquad C_2H_5.O.(NO_2). \qquad C_2H_5.O.(SO_3H).$$

The different ways of writing the formulae of ethers, such as $(C_2H_5)NO_3$, $C_2H_5.O.NO_2$, etc. are all equally justifiable.

* Ethene-thio-ethene. † Propene-thio-propene.

Monobasic acids yield only one kind of ether, "**neutral ethers**," which are analogous to the neutral salts of those acids.

Dibasic acids yield two series of ethers, (1) acid ethers and (2) neutral ethers, corresponding respectively with acid and neutral salts; thus, $C_2H_5.H.SO_4$ and $(C_2H_5)_2.SO_4$ are the acid and neutral ethyl ethers of sulphuric acid. Tribasic acids yield three series of ethers, etc.

The composition of the compound ethers is therefore exactly analogous to that of salts, so that in the definition of polybasic acids their behaviour in the formation of ethers may also be included.

The neutral ethers are mostly liquids of neutral reaction, and often of very agreeable odour, with relatively low boiling points, and volatile, eventually in a vacuum, without decomposition. Most of them are either almost or quite insoluble in water. The acid ethers, also called ether-acids, on the other hand, are of acid reaction, without smell, usually very easily soluble in water, much less stable than the neutral ethers, and not volatile without decomposition. They act as acids, *i.e.* form salts and ethers.

All compound ethers are characterized by the property of combining with water and going back again into their components, *i.e.* of undergoing "saponification," when boiled with alkalies or acids, or when heated with steam to over 100°, *e.g.* 150–180°. This sometimes takes place simply upon mixing with water at the ordinary temperature.

General modes of formation. 1. The ethers frequently result directly from their components, with elimination of water. Such a reaction, however, is only possible when the water produced by it is rendered harmless, *e.g.* by being taken up by the acid employed, for instance, concentrated H_2SO_4, HCl, or HNO_3; otherwise the ether obtained would be retransformed into its alcohol.

A direct formation of ether does not proceed quantitatively on account of the disturbing effect of the water produced in the reaction. When equivalent proportions of alcohol and acid are used, a definite point of equilibrium is arrived at which cannot be passed even upon prolonged heating; an excess of acid or alcohol increases the yield. The acid is therefore frequently allowed to act in the nascent state, by distilling a mixture of one of its salts with concentrated H_2SO_4 and the

alcohol in question; or a mixture of the alcohol and acid is allowed to drop into concentrated sulphuric acid heated to 130°, when the ether distils over; or the same mixture is saturated with gaseous hydrochloric acid. This last method is very often followed, the reaction going partly according to mode of formation 3. (Cf. also p. 99, 1.)

2. The alcohol is heated with the acid chloride, thus:

$$SO_2Cl_2 + 2C_2H_5.OH = SO(OC_2H_5)_2 + 2HCl.$$

3. The silver salt of the acid is heated with alkyl iodide, this being a method generally applicable, although it often leads to isomers of the expected ether:

$$2C_2H_5I + SO_4Ag_2 = SO_4(C_2H_5)_2 + 2AgI.$$

Besides the real acid ethers, there are also treated under this division several other classes of acid derivatives isomeric with them, but distinguished from them by not being saponifiable, *i.e.* by being more stable, *e.g.* nitro-compounds, sulphonic and phosphinic acids, etc. The hydrocyanic derivatives of the alcohols will also be described here for the sake of convenience. These latter likewise do not show the normal ether-saponifiability into alcohol and acid, but are broken up by saponifying agents in another direction.

1. Ethers of Nitric Acid.

Methyl Nitrate, $CH_3.(NO_3)$, $= CH_3.O.(NO_2)$; colourless liquid, B. Pt. 66°.

Ethyl Nitrate, or *Nitric Ether*, $C_2H_5.O.NO_2$, (*Millon*). B. Pt. 86°. Mobile liquid of agreeable odour and sweet taste, but with a bitter after-taste; burns with a white flame. Both these ethers are soluble in water. The latter is prepared directly from its components, with the addition of some urea.

Like all nitric ethers, the above compounds contain a large proportion of oxygen in a form in which it is readily given up, and they therefore explode upon being suddenly heated strongly. They saponify easily upon boiling with alkalies. Tin and hydrochloric acid reduce them to hydroxylamine:

$$C_2H_5(NO_3) + 3Sn + 6HCl = C_2H_5OH + NH_3O + 3SnCl_2 + H_2O.$$

Here also the nitrogen separates from the alcohol radicle, a reaction similar to saponification.

2. Derivatives of Nitrous Acid.

These include Nitrites and Nitro-compounds.

a. Ethers of Nitrous Acid, HNO_2.

These are obtained by the action of nitrogen trioxide or of potassium nitrite and sulphuric acid, or of copper and nitric acid upon the alcohols. They are liquids of aromatic odour, neutral reaction and very low boiling point, and are easily saponifiable. Nascent hydrogen also reconverts them into alcohol, ammonia being formed at the same time.

For *constitution*, see nitro-compounds.

Ethyl Nitrite, $C_2H_5.O.(NO)$, (*Kunkel*, 1681). Formerly called "sweet spirits of wine" or "saltpetre ether." Mobile liquid of a piercing ethereal odour, somewhat resembling that of Borsdorf apples, and of a peculiar stinging taste. B. Pt. +18°. Burns with a bright white flame. Its alcoholic solution is the officinal "Spiritus aetheris nitrosi," and is used as a taste corrective. Ethyl nitrite, as well as amyl nitrite, finds application, *e.g.* in the preparation of diazo-compounds and nitrosates (which see). For *preparation*, cf. *Wallach*, A. **253**, 251.

Methyl Nitrite, $CH_3O.NO$. Gaseous.

Amyl Nitrite, $C_5H_{11}O.NO$. B. Pt. 96°. Pale yellow liquid. Is used in medicine; it produces expansion of the blood vessels and relaxation of the contractile muscles. Isomeric with these ethers are

β. The Nitro-derivatives of the Hydrocarbons.

These are colourless liquids of ethereal odour, almost or quite insoluble in water, and boiling at temperatures up to 100° higher than their isomers. Like the latter they distil without decomposition, and occasionally explode upon being quickly heated. They are fundamentally distinguished from the nitrous ethers by not being saponifiable, and by yielding amido-compounds (see these) on reduction, the nitrogen being thus not separated:

$$CH_3.NO_2 + 3H_2 = CH_3.NH_2 + 2H_2O.$$

Nitro-methane, $CH_3.NO_2$, (*Kolbe, V. Meyer*, 1873). B. Pt. 99°–101°; Sp. Gr. > 1.

Nitro-ethane, $C_2H_5.NO_2$, (*V. Meyer* and *Stüber*, 1872). B. Pt. 113°–114°; the vapour does not explode even at a much higher temperature. Burns with a bright flame.

General modes of formation. 1. By treating alkyl iodide with silver nitrite, (*V. Meyer*), nitro-methane alone results, nitro-ethane in about an equal proportion with its isomer, and the higher homologues in regularly decreasing amounts as compared with those of their isomers, from which however they are easily separated by distillation :

$$CH_3I + AgNO_2 = CH_3.NO_2 + AgI.$$

2. Nitro-methane is further formed from mono-chloracetate and nitrite of potassium, by exchange of Cl for NO_2 and separation of CO_2, (*Kolbe*).

Nitro-compounds do not, on the other hand, result from the action of nitric acid upon the fatty hydrocarbons, or at least extremely seldom. (B. **25**, R. 108.) (Difference from the aromatic hydrocarbons.)

The *constitution* of the nitro compounds is arrived at from their not being saponifiable, and from the fact that the nitrogen is not split off on their reduction but remains directly bound to the carbon in the resulting amines, (see these). Consequently the nitrogen in them must be directly joined to the alcohol radicle, *i.e.* to the carbon, and so their constitutional formula is $R.NO_2$; for instance :

$$CH_3—N\genfrac{}{}{0pt}{}{<O}{<O}\!\!\Big| \text{, or } CH_3—N\genfrac{}{}{0pt}{}{\lessgtr O}{\;\; O}$$

according as N is taken as tri- or pentavalent.

Nitrogen which is bound directly to an alcohol radicle is therefore not separated by saponifying agents. Since the nitrogen of the isomeric nitrous ethers, on the other hand, is easily split off from the alcohol radicle either by saponification or by reduction, it is manifestly not directly combined with the carbon but only through the oxygen. The nitrous ethers therefore receive the constitutional formula R.O.(NO), *e.g.*

$$CH_3—O—N{=}O,$$

taking nitrogen as trivalent.

From this follows for the hypothetical hydrated nitrous acid the formula H.O.N:O, and for anhydride the formula $(NO)_2O$. Simultaneously we attain from this to the constitution of nitric acid. The aromatic hydrocarbons, *e.g.* benzene, C_6H_6, yield with the latter nitro-compounds, which will be treated of later on, thus :

$$C_6H_5.H + HNO_3 = C_6H_5.NO_2 + H_2O.$$

Nitric acid therefore contains a nitro-group bound to hydroxyl, corresponding with the formula:

$$H.O.NO_2 = H-O-N\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}, \text{ or } H-O-N\begin{smallmatrix}\nearrow O \searrow \\ \searrow O \nearrow\end{smallmatrix}.$$

Behaviour. 1. They yield amines with reducing agents, such as iron and acetic acid, tin and hydrochloric acid, etc., substituted hydroxylamines being formed as intermediate products (difference from the nitro-compounds of the benzene series); B. 25, 1714.

2. When the alcohol which corresponds to the nitro-compound is a primary or secondary one, so that the carbon atom which is joined to the nitro-group is at the same time joined to hydrogen, as in the groups $—CH_2.NO_2$ and $=CH.NO_2$, this hydrogen is replaceable by metals, and consequently such nitro-compounds possess the characteristics of acids.

For instance, by the action of alcoholic soda upon nitro-ethane and nitro-methane, the compounds $CH_3.CHNa.NO_2$ and $CH_2Na.NO_2$ are formed, both crystallizing in fine needles and being explosive.

The nitro-compounds of tertiary alcohols behave otherwise. Since they contain no hydrogen joined to the carbon atom which is bound to the nitro-group, they have not an acid character; the acidifying influence of the nitro-group does not therefore extend to those hydrogen atoms which are joined to other carbon atoms.

The hydrogen in the primary and secondary mono-derivatives, which is attached to the same carbon atom as the NO_2-group, can also be replaced by bromine. So long as hydrogen, as well as this bromine and the nitro-group, remains joined to the carbon atom in question, the compound is of a strongly acid character, but when it also is substituted by bromine, the compound becomes neutral; *e.g.* dibromo-nitro-ethane, $CH_3.CBr_2.NO_2$, is neutral.

3. The primary nitro-compounds yield with concentrated hydrochloric acid at 140°, acids of the acetic series containing an equal number of carbon atoms, and hydroxylamine.

4. The behaviour of the nitro-alkyls to nitrous acid is very varied. The primary yield nitrolic acids and the secondary pseudo-nitrols, while the tertiary do not react with it at all. Thus from nitro-ethane, $CH_3—C\begin{smallmatrix}\nearrow H_2 \\ \searrow NO_2\end{smallmatrix}$, "ethyl-nitrolic acid," $CH_3.C\begin{smallmatrix}\nearrow N.OH \\ \searrow NO_2\end{smallmatrix}$, an acid crystallizing in light yellow crystals and whose alkaline salts are intensely red, is formed. Normal nitro-propane acts similarly. Secondary nitro-

propane, $(CH_3)_2{=}CH(NO_2)$, gives on the contrary "propyl-pseudo-nitrol," $(CH_3)_2{=}C(NO)(NO_2)$ (?), a white crystalline, indifferent, non-acid substance, which is blue either when fused or when in solution. These reactions, which, moreover, only go on in the case of the lower molecular alcohols (in the primary up to C_8, and in the secondary up to C_5), are specially applicable for distinguishing between the primary, secondary, or tertiary nature of an alcohol (see p. 87). The nitro-hydrocarbons, which are easily prepared from the iodides, are dissolved in a solution of potash to which sodium nitrite is added, the solution acidified with sulphuric acid and again made alkaline, and then observed for the production of a red colouration (primary alcohol), a blue colouration (secondary alcohol), or no colouration at all (tertiary alcohol).

Appendix.

Chloropicrin, CCl_3NO_2, a heavy liquid of excessively suffocating smell, B. Pt. 112°, is formed from many hydrocarbon compounds by the simultaneous action of nitric acid and chlorine, chloride of lime, etc. It is best obtained from picric acid and bleaching powder.

Di-nitro derivatives of the saturated hydrocarbons, *e.g.* **Di-nitro-ethane**, $C_2H_4(NO_2)_2$, whose potassium salt is an explosive yellow crystalline compound obtained from $CH_3.CHBr(NO_2)+KNO_2$, also exist; further, some tri-nitro-derivatives, *e.g.* **Nitroform**, $CH(NO_2)_3$ (yellow crystals), and even **tetra-nitro-methane**, $C(NO_2)_4$ (white crystals), which last boils without decomposition.

3. Derivatives of Hypo-nitrous Acid.

Hypo-nitrous acid, HNO or $H_2N_2O_2$, can be transformed into an ether of the formula $(C_2H_5)_2N_2O_2$, **Diazo-ethoxane** (*Zorn*), an oil which explodes even at 40°.

4. Ethers of the Chlorine Acids

are known, *e.g.* **ethyl hypochlorite**, $C_2H_5.O.Cl$, and **ethyl perchlorate**, $C_2H_5.O.ClO_3$, both violently explosive liquids. The first of these is prepared by leading chlorine into a mixture of alcohol and aqueous caustic soda; it boils at 36°.

5. Ethers of Sulphuric Acid.

The neutral ethers are formed—

(*a*) From fuming sulphuric acid and alcohol;

(*b*) From silver sulphate and alkyl iodide;

(*c*) From sulphuryl chloride and alcohol:

$$SO_2Cl_2 + 2C_2H_5OH = SO_2(OC_2H_5)_2 + 2HCl.$$

The acid ethers or "ether sulphuric acids" of the primary alcohols result directly from their components. Secondary and tertiary alcohols do not yield them.

(*a*) **Ethyl sulphate,** $(C_2H_5)_2SO_4$, is a colourless oily liquid of an agreeable peppermint odour, insoluble in water, and solidifying on exposure to a strong cold; B. Pt. 208°. It is quickly saponified (to ordinary ether) upon warming with alcohol, also upon boiling with water, but only slowly with cold water; in the latter cases alcohol and sulphuric acid are produced.

(*b*) **Ethyl-sulphuric acid,** $C_2H_5.SO_4H$, $= C_2H_5.O.SO_3H$, (*Dabit*, 1802), is obtained from a mixture of alcohol and sulphuric acid, as given under Ethyl ether, method 1, but not quantitatively, on account of the state of equilibrium that ensues, (see p. 108). It is also formed from ethylene and sulphuric acid at a somewhat higher temperature. It differs from sulphuric acid by its Ba-, Ca-, and Pb-salts being soluble, and it can therefore be easily separated from the former by means of $BaCO_3$, etc. It yields salts which crystallize beautifully, but which slowly decompose into sulphate and alcohol on boiling their concentrated aqueous solution, especially in presence of excess of alkali. They are often used instead of ethyl iodide in the preparation of other ethyl compounds by double decomposition.

The free acid is prepared by adding the exact quantity of sulphuric acid required to the barium salt. It is a colourless oily liquid which does not adhere to glass, and which slowly decomposes into alcohol and sulphuric acid, *i.e.* is saponified, on evaporating or preserving its solution, and quickly upon boiling it.

The **methyl-, amyl-,** etc. **compounds** are analogous; the former is also a syrup which does not adhere to glass.

6. Derivatives of Sulphurous Acid.

a. Ethers of Sulphurous Acid.

(*a*) **Ethyl sulphite,** $SO_3(C_2H_5)_2$, is an ethereal liquid of peppermint odour, which can be prepared from alcohol and $SOCl_2$, and which is rapidly saponified by water.

(*b*) **Ethyl sulphurous acid,** $SO_3.H(C_2H_5)$. The very unstable potassium salt of this acid is obtained by the partial saponification of ethyl sulphite by potash solution—

$$SO_3(C_2H_5)_2 + KOH = SO_3K(C_2H_5) + C_2H_5OH.$$

The free acid is incapable of existence, decomposing immediately into its components.

Analogous ethers of other alcohols are known.

β. Sulpho- or Sulphonic Acids and their Ethers.

(*a*) **Ethyl-Sulphonic Acid,** $C_2H_5.SO_3H$ (*Löwig*, 1839; *H. Kopp*, 1840), is a strong monobasic acid, very easily soluble in water and hygroscopic, and sharply distinguished from ethyl-sulphurous acid by its stability, not being saponified upon boiling its aqueous solution either with alkalies or acids. Boiling concentrated nitric acid and free chlorine do not act upon it, and it requires fused potash to effect its decomposition. It has a strongly acid and disagreeable after-taste. It yields crystallizable salts, *e.g.* $C_2H_5.SO_3K + H_2O$ (hygroscopic), $C_2H_5.SO_3Na + H_2O$, $(C_2H_5.SO_3)_2Ba + 2H_2O$, etc.

Modes of formation. 1. From sodium or ammonium sulphite and alkyl iodide (or alkyl hydrogen sulphate; B. **23**, 908; **24**, Ref. 431):

$$C_2H_5.I + Na_2SO_3 = C_2H_5.SO_3Na + NaI.$$

2. By the oxidation of mercaptans by $KMnO_4$ or HNO_3:

$$C_2H_5.SH + 3O = C_2H_5.SO_3H.$$

3. Sulphonic ethers are formed by the action of alkyl iodide on silver sulphite:

$$2C_2H_5I + Ag_2SO_3 = (C_2H_5)_2SO_3 + 2AgI.$$

The sulphonic acids yield chlorides with PCl_5, *e.g.* ethyl-sulphonic acid gives ethyl-sulphonic chloride, $C_2H_5SO_2Cl$, a liquid which boils without decomposition at 177°, fumes in the air, and is reconverted by water into ethyl-sulphonic and hydrochloric acids. Nascent hydrogen reduces it to mercaptan.

With zinc dust it yields the zinc salt of a peculiar, syrupy, easily soluble acid, viz.—

Ethyl-sulphinic acid, $C_2H_5.SO_2H$, which is likewise converted into mercaptan upon further reduction. Its sodium salt yields ethyl sulphone when treated with ethyl bromide, C_2H_5Br. It also forms an unstable ether, isomeric with this latter compound (see p. 106; B. **24**, 2272).

Methyl-sulphonic acid, $CH_3.SO_3H$, was prepared by *Kolbe* in 1845 from trichloro-methyl-sulphonic chloride, $CCl_3.SO_2Cl$ (produced from CS_2, Cl, and H_2O). It is a syrupy liquid.

Ethyl-sulphonic ethyl ether, $C_2H_5.SO_3.C_2H_5$, is isomeric with ethyl sulphite, and, being an ether of the more stable ethyl-sulphonic acid, is only partially saponifiable. It is prepared from silver sulphite and ethyl iodide. B. Pt. 213°. The sulphonic ethers have considerably higher boiling points than the isomeric sulphurous ethers.

Constitution. From the formation of the sulphonic acids from mercaptans by oxidation, and the (indirect) reversibility of this reaction, it follows that the sulphur in them is directly bound to the alcohol radicle; if, then, sulphur is regarded as hexavalent, ethyl-sulphonic acid has the constitution

$$C_2H_5.SO_3H, = \begin{matrix} C_2H_5 \\ HO \end{matrix} > S \lessgtr \begin{matrix} O \\ O \end{matrix}.$$

From this we arrive at the constitution of sodium sulphite as being $Na-(SO_3Na)$, of the hypothetical sulphurous acid as $H-(SO_3H)$, and of sulphuric acid as $H-O-(SO_3H)$.

The real easily saponifiable sulphurous ethers therefore manifestly contain the sulphur not bound directly to the carbon but through oxygen, so that for them the following formulae hold: ethyl-sulphurous acid, $C_2H_5.O.SO_2H$, and ethyl-sulphurous acid ether, $C_2H_5O.SO.O.C_2H_5$, or $SO(OC_2H_5)_2$.

Related to methyl-sulphonic acid are: **Methane-di-sulphonic acid**, $CH_2(SO_3H)_2$, a crystalline body, **Methane-tri-sulphonic acid**, $CH(SO_3H)_3$, also crystalline, **Ethylene-** and **Ethidene-di-sulphonic acids**, $C_2H_4(SO_3H)_2$, **Propane-tri-sulphonic acid**, $C_3H_5(SO_3H)_3$, etc.; these may also be regarded as sulphurous acid derivatives of polyatomic alcohols.

7. Ethers of Tri- and Polybasic Acids.

Ethers of phosphoric acid: $PO(OR)_3$, $PO(OR)_2(OH)$, and $PO(OR)(OH)_2$, ($R =$ alkyl), exist, as do also similar compounds of phosphorous and hypophosphorous acids. The phosphinic acids, etc., are related to the two last-mentioned classes. (See phosphines.)

Ethers of boracic and silicic acids are also known.

8. Alcoholic Derivatives of Hydrocyanic Acid.

(Nitriles and Iso nitriles.)

Hydrocyanic acid, HCN, yields two classes of derivatives by the exchange of its hydrogen atom for alcohol radicles, neither of which can be grouped among the ethers, since they do not go back into alcohol and hydrocyanic acid on saponification, but decompose in another direction.

a. Cyanides of the Alcohol Radicles (Nitriles).

These are either colourless liquids, volatile without decomposition, or solids, of a not unpleasant ethereal odour slightly resembling that of leeks, lighter than water, and relatively stable. The lower members are miscible with water, but the higher ones insoluble in it. They boil at about the same temperatures as the corresponding alcohols.

Formation. 1. By heating alkyl iodide with potassium cyanide, or potassium ethyl-sulphate with potassium ferrocyanide:

$$CH_3I + KCN = KI + \underbrace{CH_3.CN}_{\text{Methyl cyanide.}}$$

2. By distillation of the ammonium salts of monobasic acids which contain one atom of carbon more than the alcohol which would be used in method 1, and treatment of the amides which are at first produced with separation of water, with a dehydrating agent such as P_2O_5, (*Hofmann*), PCl_5 or P_2S_5, (see imide chlorides and thiamides); also by treating the ammonium salts of the acids directly with P_2O_5:

$$a.\quad CH_3.COOH + NH_3 = H_2O + \underbrace{CH_3.CO.NH_2}_{\text{Acetamide.}}$$

$$b.\quad CH_3.CO.NH_2 - H_2O = CH_3.CN.$$

As a consequence of this mode of formation these compounds are also termed nitriles of the monobasic acids, *e.g.* $CH_3.CN$, methyl cyanide or Aceto-Nitrile; $C_2H_5.CN$, propionitrile, etc.

3. The higher nitriles, in which $C > 5$, result from the amides of acids of the acetic series containing one atom of

carbon more in the molecule, and also from the primary amines with the same number of carbon atoms, upon treatment with bromine and caustic soda solution (*Hofmann*). See Amides.

4. From the oximes of the aldehydes, by warming with acetic anhydride.

Behaviour. 1. These compounds are very active chemically. When heated with acids or alkalies or superheated with water, they break up into the acids from which they were originally prepared and ammonia; amides may be formed here as intermediate products:

$$CH_3.CN + 2H_2O = CH_3.COOH + NH_3.$$

This is a reaction of great moment, because it leads from the alcohols $C_nH_{2n+1}.OH$ to the acids of the acetic series, $C_nH_{2n+1}.COOH$, richer than those alcohols by one atom of carbon. (*Dumas*, *Malaguti*, *Le Blanc*, and also *Frankland* and *Kolbe*, 1847.)

2. Just as acetamide is formed by the taking up of water, so is thioacetamide by the taking up of sulphuretted hydrogen.

3. By the addition of hydrochloric acid, amido-chlorides or imido-chlorides result; by the addition of ammonia bases, amidines. Halogens also form easily decomposable addition-products (see acid derivatives).

4. Combination with hydrogen leads to amines (p. 123):

$$CH_3.CN + 2H_2 = \underbrace{CH_3.CH_2.NH_2}_{\text{Ethylamine.}}$$

5. Metallic potassium or sodium frequently induces polymerization; thus methyl cyanide yields in this way cyanmethine, a mono-acid base crystallizing in prisms.

The "official name" of the nitriles is formed by adding the word "-nitrile" to the name of the hydrocarbon containing an equal number of carbon atoms in the molecule.

For *Constitution*, see Iso-nitriles.

Aceto-nitrile (*Ethane-nitrile*), $CH_3.CN$, is present in the products of distillation from the vinasse of sugar beet and in coal tar. B. Pt. 82°; combustible, and miscible with water.

Propio-nitrile (*Propane-nitrile*), $C_2H_5.CN$, **Butyro-nitrile**, $C_3H_7.CN$, and **Valero-nitrile**, $C_4H_9.CN$, are liquids of agreeable bitter almond oil odour; **Palmito-nitrile**, $C_{15}H_{31}.CN$, is like paraffin.

Cyanogen compounds of unsaturated alcohol radicles also exist, *e.g.* **Allyl Cyanide**, $C_3H_5.CN$ (see Crotonic Acid).

Fulminic Acid. Fulminate of Mercury, $C_2HgN_2O_2$, is prepared by warming alcohol with nitric acid and mercuric nitrate (direct heating of the containing vessel by a flame is of course inadmissible). It

forms silky lustrous prisms, which explode with the utmost violence upon being heated or struck; hence it is extensively used for percussion caps, dynamite cartridges, etc. Concentrated hydrochloric acid decomposes it into formic acid and hydroxylamine. The analogous **Fulminate of Silver** is still more explosive. Free **Fulminic Acid** is unstable in the highest degree.

The constitution of fulminic acid is still a matter of doubt. Against Kekulé's formula of a nitro-acetonitrile, $CH_2(NO_2).CN$, we have, above all other arguments, the fact of its decomposition by hydrochloric acid (see above). The compound may perhaps be regarded as a polymeric oxime of carbonic oxide (B. **24**, 573); cf. also, however, *Divers*, Ch. Soc. J., **45**, 15.

β. Iso-cyanides (Iso-nitriles or Carbamines).

Colourless liquids easily soluble in alcohol and ether, but only slightly soluble or insoluble in water, of weak alkaline reaction, unbearable odour, and poisonous properties, and boiling somewhat lower than the nitriles.

Formation. 1. By heating the iodides of the alcohol radicles with silver cyanide instead of potassium cyanide, (*Gautier*), a double compound with cyanide of silver being first formed:

$$CNAg + C_2H_5I = AgI + \underbrace{C_2H_5NC.}_{\text{Ethyl iso-cyanide.}}$$

2. In small quantity, along with the nitriles, when potassium alkyl-sulphate is distilled with potassium cyanide.

3. By the action of chloroform and alcoholic potash upon primary amines, (*Hofmann*, 1869):

$$CH_3.NH_2 + CHCl_3 + 3KOH = CH_3.NC + 3KCl + 3H_2O.$$

Behaviour. 1. The iso-nitriles differ fundamentally from the nitriles by their behaviour with water or dilute acids. When strongly heated with water, or with acids in the cold, they split up into formic acid and amine bases containing one atom of carbon less than themselves, from which latter compounds they can be prepared:

$$CH_3.NC + 2H_2O = CH_3.NH_2 + HCO_2H.$$

Unlike the nitriles, they are very stable towards alkalies.

2. The iso-nitriles are also capable of forming addition products with the halogens, HCl, H_2S, etc., compounds different from those given by the nitriles; thus, with HCl they yield crystalline salts which are violently decomposed by water into amine and formic acid.

3. Some of the iso-nitriles change into the isomeric nitriles on being heated.

Methyl iso-cyanide, $CH_3.NC$. B. Pt. 58°.
Ethyl iso-cyanide, $C_2H_5.NC$. B. Pt. 82°.

Constitution of the Nitriles and Iso-nitriles. The constitution of the nitriles follows from their close relation to the acids. The carbon atom of the cyanogen group —CN remains attached to the alcohol radicle after the action of saponifying agents, and is therefore directly bound to the carbon atom of the latter. The nitrogen on the other hand is split off, and is thus not directly bound to the alcohol radicle. Consequently aceto-nitrile has the constitution : $CH_3—C{\equiv}N$.

In the case of the iso-nitriles, however, it is the nitrogen which must be directly bound to the alcohol radicle, as their close connection with the amine bases shows, the amines being easily prepared from and reconverted into the iso-nitriles. The carbon atom of the cyanogen group, on the contrary, is split off on decomposition by acid, and is consequently not bound directly to the alcohol radicle but only through the nitrogen. The constitutional formula of the iso-nitriles therefore is R—NC; either $R—N{\equiv}C$, *e.g.* methyl carbamine, $CH_3—N{\equiv}C$, etc., or $R—N{=}C{=}$, with an unsaturated carbon atom (cf. *Nef*, A. 270, 267).

The difference between nitriles and iso-nitriles is sufficiently emphasized as a rule by writing them $CH_3.CN$ and $CH_3.NC$.

D. Nitrogen Bases of the Alcohol Radicles.

By the introduction of alcohol radicles in place of hydrogen into ammonia or its salts, the important class of ammonia bases or amines and ammonium bases of the alcohol radicles is produced.

The amines containing the lower alcohol radicles bear the closest resemblance to ammonia, being even more strongly basic than the latter. They have an ammoniacal odour, give rise to white clouds with volatile acids, combine with hydrochloric acid, etc. to salts with evolution of heat, and yield double salts with platinic and gold chlorides. They further precipitate many metallic salts, the precipitates being frequently soluble in excess.

The lowest members of this class are combustible gases

readily soluble in water. The next are liquids of low boiling point, also at first easily soluble, but the solubility in water diminishes with increasing carbon (more quickly in the nitrile- than in the amido-bases), and also the volatility, until the highest members of the series, such as tricetylamine, $(C_{16}H_{33})_3N$, are at the ordinary temperature solid odourless substances of high boiling point, insoluble in water but soluble in alcohol and ether, readily combining however with acids to salts, like the others.

All amine bases are considerably lighter than water.

The ammonium bases are solid and very hygroscopic, and exceedingly like potash in properties.

Classification. The nitrogen bases of the alcohol radicles are divided into primary, secondary, tertiary, and quaternary bases, according as they contain one, two, three, or four alcohol radicles; the three first are derived from ammonia, and the last from the hypothetical ammonium hydroxide, $NH_4.OH$.

Amines or Ammonia Bases.			Ammonium Bases.
Primary or Amido-bases.	Secondary or Imido-bases.	Tertiary or Nitrile-bases.	Quaternary Bases.
$NH_2(CH_3)$ Methylamine (B. Pt. −6°).	$NH(CH_3)_2$ Di-methylamine (B. Pt. 7°).	$N(CH_3)_3$ Tri-methylamine (B. Pt. 3°).	$N(CH_3)_4I$ Tetra-methyl-ammonium iodide.
$NH_2(C_2H_5)$ Ethylamine (B. Pt. 19°).	$NH(C_2H_5)_2$ Di-ethylamine (B. Pt. 56°).	$N(C_2H_5)_3$ Tri-ethylamine (B. Pt. 89°).	$N(C_2H_5)_4OH$ Tetr-ethyl-am-monium-hydroxide.
etc.	etc.	etc.	etc.

The alcoholic radicles may be either saturated or unsaturated.

Occurrence. Some individuals of this series occur in nature, *e.g.* methylamine and tri-methylamine.

Modes of formation. 1. Methylamine, ethylamine, etc., are obtained by treating methyl or ethyl etc. iso-cyanate with potash solution (*Wurtz*, 1848):

$$CO.N(C_2H_5) + 2KOH = C_2H_5.NH_2 + K_2CO_3.$$

This method of formation yields only primary bases.

1*. The iso-thiocyanic ethers or mustard oils (see these) also yield those bases upon heating with concentrated acids.

2. By the *direct introduction of the alcohol radicle into* ammonia by heating a concentrated solution of the latter with methyl iodide, chloride, or also nitrate, ethyl iodide, etc. In this reaction an atom of hydrogen is first exchanged for an alcoholic radicle, and then the base produced combines with the halogen hydride, formed at the same time, to a salt, thus:

(I.) $$NH_2H + CH_3I = NH_2.CH_3, HI.$$

From the methylamine hydriodide thus produced, free methylamine can easily be got by distilling with potash:

$$NH_2(CH_3), HI + KOH = NH_2(CH_3) + KI + H_2O.$$

The methylamine can now combine further with methyl iodide to hydriodide of di-methylamine:

(II.) $$NH_2(CH_3) + CH_3I = NH(CH_3)_2HI,$$

which, in its turn, yields the free base with potash. This latter can again combine with methyl iodide:

(III.) $$NH(CH_3)_2 + CH_3I = N(CH_3)_3HI,$$

the salt so produced yielding tri-methylamine as before. Finally the *tri-methylamine can once more take up methyl* iodide:

(IV.) $$N(CH_3)_3 + CH_3I = N(CH_3)_4I.$$

The compound obtained, tetra-methyl-ammonium iodide, is however no longer a salt of an amine base but of an ammonium one, and is not decomposed on distillation with potash solution.

Primary and secondary bases can also be transformed into secondary and tertiary by warming with alkyl-sulphates (*e.g.* B. 24, 1678).

By using various dissimilar alkyl iodides instead of methyl iodide alone, bases are got containing different alcohol radicles together, *i.e.*, "mixed" amines, etc., *e.g.*, methyl-propylamine, $NH(CH_3)(C_3H_7)$, methyl-ethyl-propylamine, $N(CH_3)(C_2H_5)(C_3H_7)$.

The reactions I. to IV., given above, do not in reality follow each other in perfect order but go on simultaneously, the bases being partly liberated from the hydriodides by the ammonia, and so being free to react with new halogen alkyl. The product obtained by distillation with potash is therefore a mixture of all the three amine bases.

These cannot be separated by fractional distillation, and so their different behaviour with *oxalic ether*, $C_2O_2(OC_2H_5)_2$, *is made use of for* the purpose. Methylamine reacts with this ether to form chiefly (1)

di-methyl-oxamide, $C_2O_2(NH.CH_3)_2$, (solid), and (2) *some* methyl-oxamic ether, $C_2O_2(OC_2H_5)(NH.CH_3)$, (liquid); *di-methylamine* yields (3) the ethyl ether of di-methyl-oxamic acid, $C_2O_2(OC_2H_5)N(CH_3)_2$, (liquid), while tri-methylamine does not react with oxalic ether. Upon warming the product of the reaction on the waterbath, the latter base distils over, and the remaining compounds can then be separated by special methods, (for which see B. **3**, 776; **8**, 760), and individually decomposed by potash, (1) and (2) yielding methylamine, and (3) di-methylamine.

3. The nitro-compounds yield primary amido-compounds on reduction (see p. 111), thus:

$$CH_3.NO_2 + 3H_2 = CH_3.NH_2 + 2H_2O.$$

4. The nitriles, including hydrocyanic acid, are capable of taking up four atoms of hydrogen (see p. 118), and forming primary amines, (*Mendius*, 1862):

$$CH_3.CN + 2H_2 = CH_3.CH_2.NH_2 = \overbrace{C_2H_5.NH_2}^{\text{Ethylamine.}}$$

$$H.CN + 2H_2 = \overbrace{CH_3.NH_2}^{\text{Methylamine.}}$$

4a. The iso-nitriles are decomposed by hydrochloric acid, with formation of the primary amine bases from which they are also obtained (p. 119).

5. Primary amines, in which C < 6, are prepared according to *Hofmann's*, method, by the action of bromine and caustic soda solution upon the amides of acids containing one carbon atom more than themselves (see Amides).

6. Primary amines likewise result from the reduction of the oximes or hydrazones (see pp. 150, 146, and 155):

$$\underbrace{CH_3—CH=N.OH}_{\text{Aldoxime.}} + 2H_2 = CH_3—CH_2.NH_2 + H_2O.$$

Isomers. Numerous isomers exist among the amine bases, as the following table shows:

	C_2H_7N.	C_3H_9N.	$C_4H_{11}N$.
Isomers	$NH_2(C_2H_5)$ $NH(CH_3)_2$	$NH_2(C_3H_7)$ $NH(CH_3)(C_2H_5)$ $N(CH_3)_3$	$NH_2(C_4H_9)$ $NH(CH_3)(C_3H_7)$ and $NH(C_2H_5)_2$ $N(CH_3)_2(C_2H_5)$

This kind of isomerism is the same as that of the ethers (p. 101), *i.e.*, metamerism. From (C_3H_7) onwards, isomerism can also occur in the alcohol radicles. According to theory, *as many amines* C_n *as alcohols* C_{n+1} are capable of existence.

Behaviour. 1. For general behaviour, see above. When combined with acids to salts, the amines behave exactly like ammonia, and the ammonium bases like potash:

$$CH_3.NH_2 + HCl = CH_3.NH_2, HCl = (CH_3)NH_3Cl.$$
$$[N(CH_3)_4]OH + HCl = [N(CH_3)_4]Cl + H_2O.$$

The salts so obtained are white, crystalline, frequently hygroscopic compounds, easily soluble in water. The chlorides form, with platinic chloride, crystalline double compounds whose composition is analogous to that of ammonio-platinic chloride, $2NH_4Cl, PtCl_4$; *e.g.*, hydrochlorate of methylamine-platinic chloride, $2(NH_2[CH_3]HCl), PtCl_4$.

The same applies to the gold double salts, *e.g.*,

$$NH_2(C_2H_5)HCl, AuCl_3.$$

2. Saponifying agents such as alkalies and acids do not affect the nitrogen bases of the alcohol radicles, and oxidizing agents only with difficulty. (See B. 8, 1237.)

3. The different classes of amine bases are distinguished from each other by the primary having two hydrogen atoms, the secondary one, but the tertiary none replaceable by alcohol radicles; the same applies to substitution by acid radicles. The products thus resulting from isomeric amines are distinguished from one another by analysis. Thus propylamine gives with methyl iodide the base $C_3H_7N(CH_3)_2$, $= C_5H_{11}N$; the isomeric methyl-ethylamine the base $(CH_3)(C_2H_5)N(CH_3)$, $= C_4H_9N$; while tri-methylamine, $(CH_3)_3N$, $= C_3H_9N$, likewise isomeric, remains unaltered.

The primary bases further differ from the others in their behaviour with chloroform, carbon bisulphide and nitrous acid.

4. Only the primary bases react with chloroform and alcoholic potash, with formation of iso-nitriles (p. 119).

5. When warmed with carbon bisulphide in alcoholic solution, the primary and secondary, but not the tertiary bases, react to form derivatives of thio-carbamic acids. (See carbonic acid derivatives.) Should the amines be primary ones, the characteristically smelling iso-thio-cyanates are produced upon heating the thio-carbamic derivatives with a solution of $HgCl_2$, ("Senföl" reaction).

6. Nitrous acid acts upon the primary bases to reproduce the alcohols, *e.g.*:

$$CH_3.NH_2 + H.O.NO = CH_3.OH + N_2 + H_2O.$$

A molecular transformation sometimes takes place here, *e.g.* the production of iso-propyl alcohol from N-propylamine.

Secondary bases, on the other hand, yield with nitrous acid nitroso-compounds, *e.g.* "dimethyl-nitrosamine":

$$(CH_3)_2NH + NO.OH = (CH_3)_2N.NO + H_2O.$$

These nitroso-compounds are yellow-coloured liquids of aromatic odour, which boil without decomposition. (*Geuther.*) They regenerate the secondary bases upon treatment with strong reducing agents, and also upon warming with alcohol and hydrochloric acid. Weak reducing agents however convert them into hydrazines (p. 128). The nitrosamines are frequently of great service in the purification of the secondary bases.

Nitrous acid has no action upon tertiary amines.

6a. By the indirect action of nitric acid (*B.* 22, Ref. 295), *nitramines* result, *i.e.* amines in which an amido-hydrogen atom has been replaced by the nitro-group, *e.g.* $CH_3—NH—NO_2$, methyl-nitramine. Similarly, by the indirect introduction of an amido-group, hydrazines (p. 128) are formed, *e.g.* $CH_3—NH—NH_2$, methyl-hydrazine.

7. While the amine bases are liberated from their salts by alkalies, the free bases of the quaternary salts, *e.g.* tetra-methyl-ammonium iodide, cannot be prepared from these by treatment with potash, because they are as strongly basic as the latter, if not even more so. The salts however behave like hydriodates, for instance towards $AgNO_3$, and their bases, *e.g.* $N(CH_3)_4OH$, can be separated by acting upon them with moist silver oxide. They are extraordinarily like caustic potash. They cannot be distilled without decomposition, but break up on distillation with reproduction of the tertiary base, the tetra-methyl base yielding in addition methyl alcohol, and the homologous bases olefine and water, thus:

$$N(CH_3)_4.OH = N(CH_3)_3 + CH_3.OH.$$
$$N(C_2H_5)_4.OH = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

They are of great interest for the question of the valency of nitrogen, since they are more difficult to explain on the assumption of its being trivalent than pentavalent. (Cf. trimethyl-sulphine hydroxide.) The fact

that the salts $N(CH_3)_2(C_2H_5)+C_2H_5Cl$, and $N(CH_3)(C_2H_5)_2+CH_3Cl$ are identical, is in agreement with the latter assumption. (*Meyer* and *Lecco.*) Lastly, optically active isomers are met with among the quaternary ammonium salts (see p. 26), a point which receives its readiest explanation from the asymmetry of the pentavalent nitrogen.

8. The quaternary iodides go back into tertiary base and alkyl iodide upon heating. They combine with two or four *atoms of bromine or iodine to tri- and penta-bromides or* -iodides, *e.g.* $N(CH_3)_4.I.I_4$ (dark needles), and $N(C_2H_5)_4I.I_2$ (azure-blue needles). These latter must be looked upon as addition-compounds, since they readily lose their additional halogen again.

Hepta- and Ennea-iodides also exist.

Methylamine, CH_3NH_2. Occurs in *Mercurialis perennis* and annua ("mercurialin"), in the distillate from bones and wood, and in herring brine. It is produced in many decompositions of organic compounds, *e.g.* from alkaloids, as when caffeine is boiled with hydrate of baryta; also by heating hydrochlorate of tri-methylamine to 285°.

It is most easily prepared from acetamide, caustic soda and bromine. (B. **18**, 2737.) It is more strongly basic and even more soluble in water than ammonia, has a powerful ammoniacal and at the same time fish-like odour, and burns with a yellowish flame. Its aqueous solution, like that of ammonia, precipitates many metallic salts, frequently redissolving the precipitated hydroxides; unlike ammonia, it does not dissolve $Ni(OH)_2$ and $Co(OH)_2$. Below −6° it is liquid.

The hydrochlorate, $NH_2(CH_3)$, HCl, forms large glittering plates, and is very hygroscopic and easily soluble in alcohol, the platinum salt crystallizes in golden scales or hexagonal tables, the sulphate forms an alum with $Al_2(SO_4)_3+24H_2O$, and a carbonate also exists.

Methyl-nitramine, $CH_3—NH—NO_2$, has been prepared from methylurethane (B. **22**, Ref. 295). M. Pt. 38°. It has an acid character, the imido-hydrogen atom being replaceable by potassium, etc.

Di-methylamine, $(CH_3)_2NH$. Occurs in Peruvian guano and pyroligneous acid, and is formed *e.g.* by decomposing nitroso-dimethyl-aniline by caustic soda solution. B. Pt. 7°.

Tri-methylamine, $(CH_3)_3N$. Is pretty widely distributed in nature, being found in considerable quantity in Chenopodium *vulvaria*, also in *Arnica montana*, in the blossom of Crataegus oxyacantha and of pear, and in herring brine. (*Wertheim.*)

It is obtained as a decomposition product from complicated organic compounds containing nitrogen, *e.g.* from the betaïne of beetroot, and therefore along with ammonia, di-methylamine, etc., methyl alcohol and aceto-nitrile by the distillation of vinasse. It possesses an ammoniacal and pungent fish-like odour; is liquid below 3°. For its preparation see A. **267**, 254.

Tetra-methyl-ammonium iodide, $N(CH_3)_4I$, is obtained in large quantity directly from $NH_3 + CH_3I$. It crystallizes in white needles or large prisms, and has a bitter taste.

Tetra-methyl-ammonium hydroxide, $N(CH_3)_4OH$. Fine hygroscopic needles. It forms a number of salts, among others a platinum double salt, sulphide, polysulphide, cyanide, etc.; many of these are poisonous.

Ethylamine, $C_2H_5NH_2$. For its preparation by *Hofmann's* method, the crude ethyl chloride which is obtained as a bye-product in the manufacture of chloral may be used. It has a strongly ammoniacal smell and biting taste, mixes with water in every proportion with evolution of heat, and burns with a yellow flame. It dissolves $Al_2(OH)_6$ but not $Fe_2(OH)_6$, also $Cu(OH)_2$ with difficulty, but not $Cd(OH)_2$. B. Pt. 19°.

Ethyl-nitrogen chloride, $C_2H_5.NCl_2$, is a yellow oil of a most unpleasant piercing odour, obtained from the above compound with chloride of lime.

Di-ethylamine, $(C_2H_5)_2NH$, does not dissolve $Zn(OH)_2$.

Tri-ethylamine, $(C_2H_5)_3N$, is an oily strongly alkaline liquid, only slightly soluble in water. The precipitates which it gives with solutions of metallic salts are mostly insoluble in excess of the precipitant.

Vinylamine, $(C_2H_3)NH_2$. Easily decomposable.

etc. etc.

Appendix: Hydroxylamines; Hydrazines.

The **Alkyl-hydroxylamines**, which are derived from hydroxylamine, $NH_2.OH$, just as the amines are from ammonia, belong to two different series, in accordance with the constitution of hydroxylamine, thus:

$NH_2.OCH_3$	*and*	$NHCH_3.OH$
α-Methyl-hydroxylamine.		β-Methyl-hydroxylamine.

The compounds of the first series, which are obtained from the oxime-ethers (p. 150), are—as ethereal compounds—tolerably stable, and do not reduce Fehling's solution. Those of the second series, which likewise result from certain oxime derivatives, but at the same time also from the reduction of the nitro-hydrocarbons (p. 112), very readily undergo change, reduce Fehling's solution even in the cold, and pass into primary amines upon further reduction (B. **23**, 3597; **24**, 3528; **25**, 1714).

E. Fischer (A. **190**, 67; **199**, 281, 294) has given the name of hydrazines to a series of peculiar bases, mostly liquid and closely resembling the amines, but containing two atoms of nitrogen in the molecule, and differing from the latter especially by their capability of reducing *Fehling's solution*, for the most part even in the cold, and by the ease with which they are oxidized. They are derived from "Diamide" or "Hydrazine," $NH_2—NH_2$ (*Curtius* and *Jay*, J. pr. Ch. (2) **39**, 27). They result, *e.g.*, from the action of nascent hydrogen on the nitrosamines (p. 125):

$$(CH_3)_2N.NO + 2H_2 = (CH_3)_2N.NH_2 + H_2O.$$

We distinguish between primary hydrazines, $R—NH—NH_2$, and secondary, $R_2{=}N—NH_2$, according as one or both of the hydrogen atoms which are attached to an atom of nitrogen are replaced by alcohol radicles (R).

Methyl-hydrazine, $CH_3—NH—NH_2$ (Cf. A. 253, 5). An excessively hygroscopic liquid, which fumes in the air, and has an odour similar to that of methylamine. B. Pt. 87°.

Ethyl-hydrazine, $C_2H_5—NH—NH_2$. When di-ethyl urea is treated with nitrous acid, a nitroso-compound is formed, which is changed by reduction with zinc dust and acetic acid into the so-called "di-ethyl-semi-carbazide." This last decomposes upon being heated with hydrochloric acid into carbonic acid, ethylamine, and ethyl-hydrazine:

$$\underbrace{CO\begin{matrix}\diagup NH—C_2H_5\\ \diagdown NH—C_2H_5\end{matrix}}_{\text{Di-ethyl-urea.}} \quad \underbrace{CO\begin{matrix}\diagup NH—C_2H_5\\ \diagdown N(NO)—C_2H_5\end{matrix}}_{\text{Nitroso-compound.}} \quad \underbrace{CO\begin{matrix}\diagup NH—C_2H_5\\ \diagdown N(NH_2)—C_2H_5\end{matrix}}_{\text{Di-ethyl-semi-carbazide.}}$$

$$CO(NHC_2H_5)(N[NH_2]C_2H_5) + H_2O = CO_2 + NH_2C_2H_5 + NH(NH_2).C_2H_5.$$

Ethyl-hydrazine is a colourless mobile liquid of ethereal and faintly ammoniacal odour, boiling at 100°. It is very hygroscopic, forms white clouds with moist air, dissolves in water and alcohol with evolution of heat, and corrodes cork and caoutchouc.

$K_2S_2O_7$ acts upon it to form potassium ethyl-hydrazine sulphite, $C_2H_5NH—NH—SO_3K$, which in its turn reacts with mercuric oxide to yield potassium diazo-ethane sulphonate, $C_2H_5N{=}N—SO_3K$, a diazo-compound which detonates violently upon warming. (See Diazo-benzene.)

Di-ethyl-hydrazine, $(C_2H_5)_2N—NH_2$, is prepared from di-ethylamine by transforming it into di-ethyl-nitrosamine by the nitrous acid reaction, and then reducing the latter:

$$(C_2H_5)_2N—NO + 2H_2 = (C_2H_5)_2N—NH_2 + H_2O.$$

It resembles ethyl-hydrazine closely.

Tetra-ethyl-tetrazone, $(C_2H_5)_2—N—N{=}N—N—(C_2H_5)_2$, a colourless strongly basic oil, volatile with steam, results upon treating di-ethyl-hydrazine with mercuric oxide.

For the behaviour of hydrazines with aldehydes and ketones, see these; and for further particulars about hydrazine derivatives, see under *Diazo-acetic ether* and *Amido-guanidine.*

The *constitution* of the hydrazines follows from their modes of formation. Since in di-ethyl-nitrosamine, $(C_2H_5)_2N—NO$, for instance, the nitroso-group NO must be bound to the nitrogen of the amine and not to the carbon, judging from the

ease with which it can be separated, (p. 125), so the same linking of the atoms must be assumed in the hydrazines, which are formed from the nitroso-compounds by reduction, *i.e.* by exchange of O for H_2. In agreement with this stands the easy re-oxidation of the hydrazines to di-ethylamine by an alkaline solution of cupric oxide. The hydrazines are very stable as regards reducing agents.

When one H-atom in each of the two amido-groups of "Diamide" is replaced, however, hydrazo-compounds, R—NH—NH—R, are formed. (See Aromatic hydrazo-compounds.)

E. Phosphorus-, Arsenic-, etc., Compounds.

1. Phosphorus compounds of the alcohol radicles.

Just as amines are derived from ammonia, so from phosphuretted hydrogen, PH_3, are derived primary, secondary, and tertiary phosphines by the exchange of hydrogen for alcoholic radicles, and to these must likewise be added quaternary compounds, the phosphonium bases. These correspond closely with the amines in composition and in some of their properties, *e.g.* they are not saponifiable. But they differ from them in the following points :

(1) Phosphuretted hydrogen possessing hardly any basic character, they are only weak bases. Ethyl phosphine does not affect litmus and its salts decompose with water. The salts of the secondary and tertiary compounds, however, do not thus decompose, this showing that the alcohol radicles exercise a slightly basic action.

2. They also resemble phosphuretted hydrogen in being readily inflammable, and they are consequently rapidly oxidized in the air and easily take fire of themselves.

3. They are oxidized by careful addition of oxygen to acids or oxides derived from phosphoric acid, and they also combine in part with sulphur or halogen.

4. Corresponding with the disagreeable smell of phosphuretted hydrogen, they possess an excessively strong stupefying odour ; thus ethyl phosphine has a perfectly over-

powering smell, and excites on the tongue and deep down in the throat an intensely bitter taste.

Summary.

Phosphines.			Phosphonium Bases.
Primary.	Secondary.	Tertiary.	Quaternary.
$(CH_3)PH_2$ Methyl phosphine. Gas, B. Pt. −14°	$(CH_3)_2PH$ Di-methyl phosphine. Liq., B. Pt. 25°	$(CH_3)_3P$ Tri-methyl phosphine. Liq., B. Pt. 41°	$(CH_3)_4PI$ and $(CH_3)_4P.OH$ Tetra-methyl-phosphonium-hydroxide.
Spontaneously inflammable.		Fuming.	Similar to potash.
Yield upon oxidation			
with fuming nitric acid.		in the air.	Yields upon heating CH_4 and ← (tertiary phosphine oxide)
$(CH_3)PO(OH)_2$ Methyl-phosphonic acid.	$(CH_3)_2PO(OH)$ Di-methyl-phosphinic acid.	$(CH_3)_3PO$ Tri-methyl-phosphine oxide.	
Like paraffin.		Hygroscopic needles.	
M. Pt. 105°	M. Pt. 76°	B. Pt. 240°	

Formation. 1. The tertiary phosphines, and also quaternary compounds, result directly from phosphine and alkyl iodide, in a manner analogous to method of formation 2 of the amines :

$$PH_3 + 3C_2H_5I = P(C_2H_5)_3 + 3HI.$$

2. According to *Hofmann* (1871), primary and secondary phosphines are formed by heating phosphonium iodide and alkyl iodide with zinc oxide, *e.g.* :

$$2C_2H_5I + 2PH_4I + ZnO = 2P(C_2H_5)H_2,\ HI + ZnI_2 + H_2O.$$

They can be separated from one another by decomposing the salts of the primary phosphines by water, as already mentioned.

3. The tertiary phosphines are produced from calcium phosphide and alkyl iodide, a reaction first observed by *Thenard* in 1846 ;

4. Also from phosphorus trichloride and zinc methyl.

5. The phosphonium compounds result from the combination of tertiary compounds with halogen alkyl, and are very similar to the corresponding ammonium compounds.

Methyl phosphine, $CH_3.PH_2$, (*Hofmann*), is of neutral reaction and easily soluble in alcohol and ether; its salts bleach vegetable colours. It is spontaneously inflammable.

Tri-methyl phosphine, $P(CH_3)_3$, changes in the air into Tri-methyl-phosphine oxide, $P(CH_3)_3O$, which distils without decomposition and is very stable in character. The phosphine also forms with sulphur a sulphide analogous to the oxide, and with chlorine a di-chloride, and it combines with carbon bisulphide to a compound crystallizing in red plates. This last reaction is very delicate, (*Hofmann*).

Tetra-methyl-phosphonium Hydroxide, $P(CH_3)_4OH$. Unlike the analogous ammonium hydroxide this compound decomposes upon heating into tri-methyl-phosphine oxide and methane:

$$P(CH_3)_4OH = P(CH_3)_3O + CH_4.$$

The tetra-ethyl compound breaks up in the same way.

Tri-ethyl phosphine, $P(C_2H_5)_3$, has no alkaline reaction. When concentrated it possesses a stupefying, and when dilute a pleasant hyacinth-like odour.

The tendency of phosphorus to go over into the pentavalent state shows itself in characteristic fashion in these compounds. The group $P(CH_3)_4$ is a strongly positive monovalent, and the group $P(CH_3)_3$ a strongly positive divalent radicle, the former being comparable with the alkalies and the latter with the alkaline earth metals. The metalloid character of phosphorus is therefore changed into one more metallic by the advent of the alkyl groups.

The phosphonic acids, phosphinic acids and phosphine oxides above-mentioned can be derived from phosphoric acid by the exchange of OH for alkyl, thus:

$$PO\begin{cases}OH\\OH\\OH\end{cases} \qquad PO\begin{cases}C_2H_5\\OH\\OH\end{cases} \qquad PO\begin{cases}C_2H_5\\C_2H_5\\OH\end{cases} \qquad PO\begin{cases}C_2H_5\\C_2H_5\\C_2H_5\end{cases}$$

Phosphoric acid.	Ethyl-phosphonic acid.	Di-ethyl-phosphinic acid.	Tri-ethyl-phosphine oxide.

The first may also be regarded as alcoholic derivatives of phosphorous and hypophosphorous acids, but not as ethers of these, since they are not saponifiable.

2. Arsenic Compounds of Alcohol Radicles.

Type.	Arsines.			Arsonium Bases.
	Primary.	Secondary.	Tertiary.	Quaternary.
1. $AsCl_3$	$AsCl_2(CH_3)$ Methyl-arsine dichloride. Liq., B. Pt. 133°	$AsCl(CH_3)_2$ Cacodyl chloride Liq., B. Pt. 100°	$As(CH_3)_3$ Tri-methyl arsine. Liq., B. Pt. 70°	$As(CH_3)_4 . OH$ Tetra-methyl-arsone hydroxide; like potash. $As(CH_3)_4I$ Tetra-methyl-arsone iodide. Tables. $As(CH_3)_4Cl$ Tetra-methyl-arsone chloride.
2. $AsCl_5$	Chlorine Addition-compounds.			
	$AsCl_4(CH_3)$ Methyl-arsine-tetrachloride.	$AsCl_3(CH_3)_2$ Cacodyl trichloride.	$AsCl_2(CH_3)_3$ Tri-methyl-arsine dichloride	

Corresponding Oxides.

3. As_2O_3	$As(CH_3)O$ Methyl-arsine oxide. Prisms, M. Pt. 95°	$\{As(CH_3)_2\}_2O$ Cacodyl oxide. Liquid, B. Pt. 150°		
4. $AsO(OH)_3$	$(CH_3)AsO(OH)_2$ Methyl-arsonic acid. Tables.	$(CH_3)_2AsO(OH)$ Cacodylic acid. Prisms, M. Pt. 200°	$(CH_3)_3AsO$ Tri-methyl-arsine oxide. Crystals.	

The similarity of arsenic to phosphorus and nitrogen is further exemplified by the analogous compounds which it forms with alcohol radicles. In virtue, however, of the more metallic character of arsenic, these compounds differ from the others by the arsenic not being able to combine with hydrogen

together with alcohol radicles, but only with electro-negative elements like chlorine or oxygen. Arsenic analogues of methylamine and di-methylamine have therefore no existence, but we know tri-methyl-arsine, analogous to tri-methylamine and tri-methyl-phosphine. As primary and secondary compounds we have methyl-arsine dichloride, $CH_3.AsCl_2$, di-methyl-arsine chloride, $(CH_3)_2{=}AsCl$, and analogous substances.

They are colourless liquids of stupefying odour, exerting in some cases an unbearable irritating action upon the mucous membrane. They do not possess basic properties. In addition to these there exist also quaternary compounds which are exactly analogous to the quaternary phosphonium ones.

The halogen of the chlorine compounds is easily replaceable by its equivalent of oxygen. Thus, corresponding to the compound $R.AsCl_2$ there is an oxide R.AsO and a sulphide R.AsS, and to the chloride R_2AsCl an oxide $(R_2As)_2O$. (See tabular summary, row 3.) These oxides, liquid or solid, are compounds of stupefying odour, and behave like basic oxides; HCl reconverts them into the chlorides of row 1.

Here, also, the tendency of arsenic to change from the—(apparently)—trivalent to the pentavalent state is especially marked. The above chlorides and tri-methyl-arsine itself all combine with two atoms of chlorine to compounds of the type AsX_5, (see table, row 2). The above oxygen compounds of the type AsX_3 and also tri-methyl-arsine are consequently oxidizable to compounds containing one O-atom or two OH-groups more, acids or oxides which are also formed from the chlorides of the type AsX_5 by exchange of halogen for O or OH, *e.g.* cacodyl oxide, $(R_2As)_2O$, to cacodylic acid, $R_2As.OOH$, (see table, row 4). These products are therefore completely analogous to the phosphonic and phosphinic acids and phosphine oxides already described.

The compounds $As(CH_3)_xCl_{5-x}$, of the type AsX_5, break up upon heating into methyl chloride and compounds $As(CH_3)_{x-1}Cl_{4-x}$, of the type AsX_3, this separation of methyl chloride taking place the more readily the fewer methyl

groups are present in the molecule; thus $As(CH_3)_3Cl_2$ breaks up when somewhat strongly heated, $As(CH_3)_2Cl_3$ at 50°, and $As(CH_3)Cl_4$ at 0°, *i.e.* the last-named is only stable when in a freezing mixture. When, therefore, chlorine acts upon $As(CH_3)Cl_2$ at the ordinary temperature, the reaction appears to be one of direct exchange of alkyl for chlorine, thus:

$$As(CH_3)Cl_2 + Cl_2 = AsCl_3 + CH_3Cl.$$

If one considers arsenic to be a trivalent element, one finds support for this view in the fact of $AsCl_5$ having no existence, and $As(CH_3)_5$ only a doubtful one; the compounds of the type AsX_5 are in this case to be regarded as molecular compounds of $AsX_3 + Cl_2$. The adding on of the chlorine molecule would thus be conditioned by the latent affinities of the chlorine to the arsenic and to the alcohol radicle, which indeed finds expression in the separation of chloro-alkyl at an increased temperature.

It is interesting to note that, like free "methyl" (CH_3—) the radicle —$As(CH_3)_2$ has no separate existence; cacodyl possesses the doubled formula $As_2(CH_3)_4$ ("Di-arsene-dimethyl").

Modes of formation. A. The *tertiary arsines* result:

1. From sodium arsenide and alkyl iodide, (*Cahours* and *Riche*).

$$AsNa_3 + 3C_2H_5I = As(C_2H_5)_3 + 3NaI.$$

2. From zinc alkyl and arsenic trichloride, (*Hofmann*).

Tri-methyl-arsine, $As(CH_3)_3$, and **tri-ethyl-arsine**, $As(C_2H_5)_3$, are liquids difficultly soluble in water. They fume in the air, changing thereby into tri-methyl- or -ethyl-arsine oxide, with evolution of heat.

B. The **secondary arsines** are obtained from cacodyl and cacodyl oxide, which result from the distillation of potassium acetate and arsenic trioxide, (*Cadet*, 1760):

$$O\left\{\begin{matrix}AsO\\AsO\end{matrix}\right. + 4CH_3.CO_2K = O\left\{\begin{matrix}As(CH_3)_2\\As(CH_3)_2\end{matrix}\right. + 2CO_2 + 2CO_3K_2.$$

The distillate of cacodyl and cacodyl oxide so obtained, and termed "alkarsin," fumes in the air and is spontaneously inflammable. (*Cadet's* "fuming arsenical liquid.") Hydrochloric acid acts upon it to form cacodyl chloride (*Bunsen*, 1838), and caustic potash solution gives pure **Cacodyl oxide**, $As_2(CH_3)_4O$, a liquid of stupefying odour which produces nausea and unbearable irritation of the nasal mucous membrane; it boils without decomposition, and is insoluble in water and of neutral reaction.

It yields salts with acids, *e.g.* **Cacodyl chloride** with hydrochloric acid:

$$\{(CH_3)_2As\}_2O + 2HCl = 2(CH_3)_2As.Cl + H_2O.$$

This latter compound is a liquid of even more stupefying odour and violent action than the former, and whose vapour is spontaneously inflammable. Upon being heated with zinc clippings in an atmosphere of carbonic acid, it yields the free **Cacodyl**, $As_2(CH_3)_4$ (from κακώδης, "stinking"), a colourless *liquid insoluble in water and boiling undecomposed at 170°*, of a horrible nauseous odour which produces vomiting. It is as easily inflammable in the air as the vapour of phosphorus, yielding the oxide when slowly brought in contact with it, and also combining directly with sulphur, chlorine, etc. Cacodyl plays, therefore, even down to the móst minute particulars, the part of a simple electro-positive element; it is a true "organic element," (*Bunsen*).

Cacodylic acid, $(CH_3)_2AsO.OH$, is crystalline, soluble in water, odourless and poisonous. It forms crystallizable salts.

C. The *primary arsines* or mono-alkyl-arsenic compounds(*Baeyer*, 1858), result from **Alkyl-arsine dichloride,** *e.g.* CH_3AsCl_2, which on its part is obtained by heating cacodyl trichloride, with separation of CH_3Cl. It is a heavy liquid, soluble in water without decomposition, and also boiling undecomposed, its vapour having a terribly aggressive action.

3. Antimony, Boron, and Silicon compounds.

Antimony also forms compounds with the alkyls precisely similar to those of arsenic; primary and secondary compounds do not exist. **Tri-methyl-stibine,** $Sb(CH_3)_3$ (*Landolt*), is a highly disagreeable and spontaneously inflammable liquid of onion-like smell; and **Antimony penta-methyl,** $Sb(CH_3)_5$, an oily liquid of weak odour, which can be distilled, and is not spontaneously inflammable. **Tetra-methyl-stibonium-hydroxide,** $Sb(CH_3)_4OH$, is also very like caustic potash.

Boron tri-ethyl, $Bo(C_2H_5)_3$ (*Frankland*), *is a spontaneously inflammable* liquid which burns with a green flame with deposition of much soot, and **Boron tri-methyl,** $Bo(CH_3)_3$, an analogous gas of an unbearable stinking smell.

The Silicium compounds (*Friedel* and *Crafts*) are, in contradistinction to the foregoing, not like the easily spontaneously inflammable silicon hydride, but like methane and the paraffins, and are very stable in the air, *i.e.* not spontaneously *inflammable.*

Silicium tetra-methyl, $Si(CH_3)_4$, is a mobile liquid similar to pentane, which swims upon water.

F. Metallic Compounds of the Alcohol Radicles.

The alcohol radicles can be combined with almost all the more important metals. The composition of the compounds so formed, termed organo-metallic or metallo-organic compounds, almost always corresponds with that of the metallic chlorides from which they are derived by the replacement of halogen by alkyl. They are colourless mobile liquids which boil without decomposition at relatively low temperatures; they often decompose violently with water and burn explosively in the air, but in other cases they are stable, both in water and air. To the former category belong the magnesium, zinc and aluminium alkyls, and to the latter the mercury, lead and tin compounds.

Compounds are also known which contain halogen as well as alcohol radicle combined with a metal. They behave like salts. The halogen in them can be replaced by hydroxyl, whereby basic compounds result, compounds which are often much more strongly basic than the corresponding metallic hydroxides, in accordance with the electro-positive character of the alcohol radicle. Such hydroxides or oxides cannot be volatilized without decomposition.

Modes of formation. 1. By treating the halogen-alkyl with the metal in question. In this way zinc-, magnesium- and mercury-alkyl are got:

$$Mg_2 + 2CH_3I = Mg(CH_3)_2 + MgI_2.$$

2. By treating zinc-alkyl or mercury-alkyl with the metal. One thus obtains *e.g.* cadmium ethide and potassium methide:

$$Hg(CH_3)_2 + Cd = Cd(CH_3)_2 + Hg.$$

3. By double decomposition between zinc-alkyl and the chloride of the metal:

$$2Zn(C_2H_5)_2 + SnCl_4 = Sn(C_2H_5)_4 + 2ZnCl_2.$$

Potassium- and Sodium methide, $K(CH_3)$ and $Na(CH_3)$, and **Potassium- and Sodium ethide**, $K(C_2H_5)$ and $Na(C_2H_5)$, are

not known in the free state. When metallic sodium is added to zinc ethyl (or ethide), zinc separates out and a crystalline compound of sodium ethide and zinc ethide is formed, from which, however, the former cannot be prepared pure, since decomposition sets in upon warming. On distilling in a stream of carbonic acid, the potassium methide combines with the latter to form potassic acetate; the ethyl compound behaves in a similar way.

Zinc methyl or **methide**, $Zn(CH_3)_2$, (*Frankland*, 1849). This important compound is, like the other zinc alkyls, prepared according to method 1, the reaction taking place in two stages:

$$\text{I. } CH_3I + Zn = Zn(CH_3I);$$
$$\text{II. } 2Zn(CH_3)I = Zn(CH_3)_2 + ZnI_2.$$

The first stage is completed upon warming, and the second upon distilling the resulting product. The zinc is conveniently used in the form of the "*copper-zinc couple*," and the reaction is facilitated by the addition of acetic ether, the reason for this not being known. Zinc methyl is a colourless, mobile, strongly refracting liquid of very piercing and repulsive smell. B. Pt. 46°; Sp. Gr. 1·39. It takes fire in the air at once, and burns with a brilliant reddish-blue flame (the zinc flame), with formation of zinc oxide. When the supply of oxygen is limited, zinc methylate, $Zn(OCH_3)_2$, is formed. It decomposes violently with water to methane and $Zn(OH)_2$, and gives ethane with methyl iodide. It is employed *e.g.* in the preparation of secondary and tertiary alcohols and of acetone. Iodine converts it into **Zinc-methyl iodide**, $ZnCH_3I$, white plates, (see above), and methyl iodide; an excess of iodine yields zinc iodide and methyl iodide.

Zinc ethide, $Zn(C_2H_5)_2$, B. Pt. 118°, Sp. Gr. 1·18, is exactly like zinc methide.

Mercury methide, $Hg(CH_3)_2$, (*Frankland*), and **Mercury ethide**, $Hg(C_2H_5)_2$, (*Buckton*), are produced by method of formation 1, also by method 3. They are colourless liquids of peculiar sweetish and unpleasant odour. B. Pt. of the methyl compound 95°, and Sp. Gr. $>$3. B. Pt. of the ethyl compound 159°. They are permanent in the air but inflammable, and both—especially the methyl compound—

are very poisonous. HCl reacts to produce **Mercury-methyl chloride**, $Hg(CH_3)Cl$, a colourless salt, thus:

$$Hg(CH_3)_2 + HCl = Hg(CH_3)Cl + CH_4.$$

To this there is a corresponding iodide and also a hydroxide, $Hg(CH_3)OH$, of strongly alkaline reaction.

Mercury-ethyl hydroxide, $Hg(C_2H_5)OH$, is an oily odourless liquid of extremely caustic taste, slippery to the touch like potash, and gradually blistering the skin.

Aluminium methide, $Al(CH_3)_3$, is spontaneously inflammable and decomposes violently with water. B. Pt. 130°. For Vap. Dens. see B. **22**, 551. **Cadmium** and **Magnesium methides** are also known.

Lead methide, $Pb(CH_3)_4$, and **ethide**, $Pb(C_2H_5)_4$ (*Cahours*). These are formed according to method 3, curiously with separation of lead:

$$2PbCl_2 + 2Zn(CH_3)_2 = Pb(CH_3)_4 + Pb + 2ZnCl_2.$$

They are stable in the air, and are interesting from the lead in them being tetravalent. The **Hydroxide**, $Pb(CH_3)_3.OH$, forms pointed prisms, smells like mustard, and is a strong alkali; thus, it saponifies fats, drives out ammonia from its salts, precipitates metallic salts, etc. The compound $Pb_2(C_2H_5)_6$ is also known.

The tin compounds are similar (*Ladenburg*, *Frankland*).

Tin tetra-methide, $Sn(CH_3)_4$, **Tin tetra-ethide**, $Sn(C_2H_5)_4$, **Tin tri-ethide**, $Sn_2(C_2H_5)_6$, **Tin di-methide**, $Sn_2(CH_3)_4$, etc., are of interest as proving the tetravalence of tin.

V. ALDEHYDES AND KETONES, $C_nH_{2n}O$.

The aldehydes and ketones are substances which result from the oxidation of the primary and secondary alcohols respectively, with separation of two atoms of hydrogen.

The Aldehydes are formed from the primary alcohols, and are easily converted by further oxidation into the corresponding acids containing an equal number of carbon atoms, oxygen being taken up. They possess in consequence strongly reducing properties.

The Ketones result from the oxidation of the secondary alcohols, and are more difficult to oxidize further; they do not possess reducing properties. Their oxidation does not lead to acids containing an equal number of carbon atoms in the molecule, but to others containing a smaller number, the carbon chain being broken.

The lower members of both classes are neutral liquids of peculiar smell, easily soluble in water and readily volatile, only CH_2O being gaseous. With increasing carbon they soon become insoluble in water, and their odour becomes less marked with rise of melting point until the highest members are solid, odourless, like paraffin, and only capable of being distilled without decomposition in a vacuum.

The aldehydes are also perfectly analogous to the ketones as regards other modes of formation and in many of their properties.

A. Aldehydes.

The homologous series of the aldehydes, $C_nH_{2n}O$, corresponds exactly with that of the acids, $C_nH_{2n}O_2$. Their boiling points lie decidedly lower than those of the corresponding alcohols, and rise, in the normal aldehydes, at first by about 27° for each CH_2, and later on by a less amount.

Modes of formation. 1. By the regulated oxidation of the primary alcohols, $C_nH_{2n+1}OH$, by potassium bichromate or manganese dioxide and dilute sulphuric acid; often slowly by the oxygen of the air alone, especially in the presence of bone black or platinum:

$$\underbrace{CH_3.CH_2OH}_{\text{Alcohol.}} + O = \underbrace{CH_3.CHO}_{\text{Acetic aldehyde.}} + H_2O.$$

Aldehydes are also produced by the oxidation of many complicated organic substances, such as albumen.

2. From the acids of the acetic series, by distilling a mixture of their calcium or barium salts with calcium or barium formate, (*Limpricht*). The formic acid acts in this instance as a reducing agent, producing calcium carbonate, thus:

$$CH_3.COOca + HCOOca = CH_3.CHO + CaCO_3. \quad (ca = \tfrac{1}{2}\,Ca.)$$

Other reducing agents have for the most part no action.

3. From the di-halogen substitution products of the hydrocarbons containing the atomic group CHX_2, by superheating with water or by boiling with water and PbO:

$$\underbrace{CH_3{-}CHCl_2}_{\text{Ethylidene chloride.}} + H_2O = CH_3{-}CHO + 2HCl.$$

Constitution. By the oxidation of the primary alcohols, $R—CH_2.OH$, to their corresponding acids, whose constitution follows as $R—CO.OH$, the new oxygen atom affixes itself only to that carbon atom which is already combined with oxygen—in the form of hydroxyl—, the hydrocarbon radicle R remaining unaltered. It must consequently also remain unchanged in the intermediate products of the oxidation, the aldehydes, which therefore possess the constitution $R—CHO$:

$CH_3—CH_2.OH$	$CH_3—CHO$	$CH_3—CO.OH$
Alcohol.	Aldehyde.	Acetic acid.

The aldehydes thus contain the atomic group $—CHO$ or $—C\lt^{O}_{H}$, bound either to hydrogen as in formic aldehyde, $H—CHO$, or to an alcohol radicle as in all the other cases.

Isomers. Isomerism in the aldehydes is caused solely by isomerism in the alcohol radicles R, which are combined in them with the group $—CHO$, and therefore contain an atom of carbon less. Otherwise the aldehydes—from C_3H_6O on—are isomeric with the ketones, with the oxides of the olefines (*e.g.* aldehyde with ethylene oxide, C_2H_4O), and with the alcohols of the allylic series.

The "official names" (p. 28) of the Aldehydes end in "al."

Behaviour. The aldehydes are distinguished by being exceptionally active chemically.

1. For oxidation, see above. The aldehydes are very readily oxidizable, slowly even by the air alone, and quickly by chromic acid, salts of the noble metals, etc. They consequently reduce an ammoniacal solution of silver and often one of copper; this reaction is characteristic and is especially delicate in the presence of caustic soda solution.

2. The aldehydes are easily reducible by nascent hydrogen, *e.g.* sodium amalgam and dilute acid or zinc dust and glacial acetic acid, to the primary alcohols from which they are derived by oxidation, *e.g.*:

$$CH_3—CHO + H_2 = CH_3.CH_2OH.$$

A glycol is formed as intermediate product, *e.g.* butylene glycol, $C_4H_8(OH)_2$, from C_2H_4O.

3. Phosphorus pentachloride and -trichloride convert the aldehydes into ethylidene chloride and analogous di-chloro-substitution products of the hydrocarbons.

4. Addition-reactions. One would expect that upon treating ethylidene chloride or analogous chlorides with water and lead oxide, for instance, two hydroxyl groups would replace two chlorine atoms, and a compound, $CH_3—CH<^{OH}_{OH}$, would be produced, which would be a diatomic alcohol, "ethylidene glycol." Such compounds are however not formed, being apparently broken up at once into aldehyde and water, thus:

$$CH_3—CH<^{OH}_{OH} = CH_3—CHO + H_2O.$$

From this we may draw the conclusion *that two hydroxyl groups bound to one and the same carbon atom cannot as a rule exist together*, but a molecule of water is separated, and an oxygen atom is bound by its two affinities instead. Only in particular cases are compounds with two such hydroxyls capable of existence (see below), being formed by the addition of water to the aldehyde in question.

If, in place of water, $NaHSO_3$, NH_3, HCN, etc., be employed, direct addition to the aldehydes is observed, and this is to be explained in every case by the doubly-linked oxygen atom loosening one of its affinities from the carbon, so that an affinity remains free in the case of both of them, thus:

$$CH_3—CH<^{O—}, \text{ or, generally, } R—CH<^{O—}.$$

A hydrogen atom of the substance in question now affixes itself to the oxygen of the aldehyde, with formation of a hydroxyl group, while the residual X, *e.g.* NH_2, which was originally bound to the afore-mentioned H-atom, attaches itself to the carbon; these compounds receive therefore the formula:

$$CH_3—CH<^{OH}_{X} .$$

The substances so produced are to be regarded as derivatives, such as simple and compound ethers, amines, etc., of the hypothetical ethylidene- and homologous glycols.

The most important addition-reactions are as follows:—

(*a*) Combination with water, which would lead to a diatomic alcohol, does not as a rule take place, for the reasons already given. Should the alcohol radicle of the aldehyde, however, contain several negative atoms, *e.g.* Cl, then the hydrates are capable of existence, for instance chloral hydrate:

$$CCl_3—CHO + H_2O = CCl_3—CH(OH)_2.$$

But even in these cases the tendency for water to separate is too great to allow of such hydrates behaving as diatomic alcohols; they react rather, for the most part, exactly like the aldehydes themselves. (Cf. pyroracemic and mesoxalic acids.)

(*b*) Similarly, combination but seldom takes place with alcohol, acetic acid, etc., with the formation of an easily decomposable alcoholate or acetate. But, upon heating with alcohol or acetic anhydride, stable ethers, simple and compound, of the hypothetical glycols are obtained:

$$CH_3—CHO + 2C_2H_5.OH = CH_3—CH(OC_2H_5)_2 + H_2O.$$
$$CH_3—CHO + (C_2H_3O)_2O = CH_3—CH(OC_2H_3O_2)_2.$$

The compounds resulting from alcohols, the so-called "acetals" (see p. 148), are also formed by the partial oxidation of primary alcohols, and are again separated into their components by sulphuric acid.

Thio-alcohols (p. 102), yield with aldehyde, under the influence of gaseous HCl, thio-acetals which are termed **Mercaptals** (*Thials*).

(*c*) The aldehydes combine with sodium bisulphite, $NaHSO_3$, ammonium bisulphite, etc., to crystalline compounds, easily soluble in water but difficultly in alcohol, *e.g.*

$$C_2H_4O + NaHSO_3 + \tfrac{1}{2}H_2O.$$

These are to be regarded as sulphonic acids of the ethylidene- etc., glycols, for instance, $CH_3—CH(OH)(SO_3Na)$. Nevertheless they are almost always easily broken up again with re-formation of the aldehyde, warming with soda solution or with acids effecting this. They are therefore of great importance for the separation of aldehydes from mixtures.

(*d*) The aldehydes combine with ammonia to aldehyde-ammonias, *e.g.* **Aldehyde-ammonia**, $CH_3—CH(OH)(NH_2)$. These

are crystalline compounds, for the most part easily soluble in water, difficultly in alcohol, and insoluble in ether, which go back into the original aldehyde when warmed with dilute acids. Like the bisulphite compounds, they are advantageously used for the preparation of pure aldehydes. (See p. 147.)

Imido-compounds of the aldehydes, $R—CH=NH$, are only known in a few instances, *e.g.* chloral-imide, $CCl_3—CH=NH$. On the other hand the aldehydes unite with *primary amines*, water being eliminated; for instance, ethyl-methylene-amine, $CH_2=N—C_2H_5$, results from trioxy-methylene (p. 147) and ethylamine. From *aromatic primary amines*, compounds of the type $R—CH(NHR)_2$ are frequently obtained.

Many nitrile compounds are known, *e.g.* Hydracetamide $(CH_3-CH)_3N_2$.

(*e*) The aldehydes combine with hydrocyanic acid to form nitriles of higher acids, thus, acetic aldehyde yields the compound $CH_3—CH\langle^{OH}_{CN}$, **ethylidene cyanhydrin**, a liquid easily broken up again into its components. (See lactic acid.)

5. The aldehydes show great tendency to polymerize. (See pp. 14 and 57.) In the case of formic aldehyde this polymerization sets in of its own accord at the ordinary temperature. Acetic aldehyde is polymerized upon the addition of small quantities of hydrochloric, sulphuric, or sulphurous acid, zinc chloride, carbonyl chloride, etc., to para-aldehyde, $C_6H_{12}O_3$, $= (C_2H_4O)_3$, at the ordinary temperature, and to meta-aldehyde, $(C_2H_4O)_x$, at 0°. Why the above-mentioned substances should induce this polymerization is not known.

6. Towards alkalies the aldehydes behave differently. Aldehyde and several of its homologues are converted by heating with caustic soda solution into a reddish-brown resin termed **aldehyde-resin**, insoluble in water but soluble in alcohol, a peculiar odour being apparent at the same time. This reaction is characteristic. Other aldehydes are transformed by alkalies into a mixture of equal molecules of alcohol and acid, the one half being oxidized at the cost of the other half, thus:

$$2HCOH + H_2O = CH_3OH + H.CO_2H \text{ (Formic acid).}$$

7. The aldehydes show great inclination to form condensation products, *i.e.* two molecules may combine together with a rearrangement of the carbon bonds and formation of a compound containing twice as many atoms of carbon, a hydrogen

atom of the one molecule combining with the oxygen of the other to hydroxyl.

In this way, when aldehyde stands for a lengthened period with dilute hydrochloric acid or soda solution, **β-oxy-butyric aldehyde** (see **Aldol**) is formed; this is termed an "aldol condensation:"

$$CH_3—CHO + CH_2H—CHO = CH_3—CH(OH)—CH_2—CHO.$$

Aldol condensation. Aldol readily separates water and goes into **Crotonic aldehyde**, $CH_3—CH=CH—CHO$, which also results directly upon warming aldehyde with zinc chloride ("Aldehyde condensation"). Sulphuric acid, sodium acetate in aqueous solution, and alkalies, *e.g.* dilute soda, baryta water, etc., also induce condensation.

The "aldol condensation" is easily explained by assuming the formation of an aldehyde hydrate, and subsequent separation of one of the two hydroxyls thus formed with a hydrogen atom of a second aldehyde molecule. For condensation with ketones, see these.

7*a*. The aldehydes combine in a similar manner with sodium acetate and acetic anhydride to acids poorer in hydrogen. See *e.g.* Cinnamic acid.

8. Chlorine and bromine act upon the aldehydes as substituents; thus, from acetic aldehyde chloral is obtained:

$$CH_3—CHO + 3Cl_2 = CCl_3—CHO + 3HCl.$$

9. Sulphuretted hydrogen converts the aldehydes into thioaldehydes. These are compounds of unpleasant aromatic odour, which show the same peculiarities of polymerization as the aldehydes (*Klinger*). Cf. *E. Baumann*, B. **23**, 60; **24**, 1419, 3591.

10. With hydroxylamine the aldehydes yield the so-called **Aldoximes**, water being separated, *e.g.* aldoxime, $CH_3—CH=N.OH$ (*V. Meyer*, B. **15**, 2778).

$$CH_3.CHO + NH_2OH = CH_3.CH=N.OH + H_2O.$$

For the conditions under which oximes are formed, see B. **23**, 2769.

11. The aldehydes react with hydrazines to form the so-called "*Hydrazones*," water being eliminated (*E. Fischer*), for instance:

$$CH_3—CH=N_2HC_2H_5, \text{ acetaldehyde-ethyl-hydrazone.}$$

This reaction goes particularly well with phenyl-hydrazine, thus:

$$CH_3—CHO + C_6H_5—NH—NH_2 = \underbrace{CH_3—CH=N_2H—C_6H_5}_{\substack{\text{Aldehyde-phenyl-hydrazone} \\ \text{(Ethane-phenyl-hydrazone).}}} + H_2O.$$

The hydrazones are broken up by reduction, with formation of primary amines, *e.g.*

$$CH_3—CH=N_2H—C_6H_5 + 2H_2 = CH_3—CH_2.NH_2 + NH_2.C_6H_5.$$

For further details see Phenyl-hydrazine.

Tests for aldehydes:

(1) Behaviour with ammoniacal silver solution (p. 141, and also B. **15**, 1629).

(2) Behaviour with alkaline bisulphites (p. 143).

(3) Behaviour with phenyl-hydrazine and hydroxylamine (see above).

(4) Aldehydes colour a solution of fuchsine, which has been decolourized by sulphurous acid, an intense violet-red; some ketones and chloral, but not chloral hydrate, produce the same effect. *Schiff, Caro* (B. **13**, 2343).

Formic Aldehyde (*Methanal*), *Methyl Aldehyde*, H.CHO. This may also be regarded as the oxide of the diatomic radicle methylene, $CH_2=$. It is obtained dissolved in excess of methyl alcohol by leading the vapour of the latter, mixed with air, over a glowing platinum or copper spiral or platinum asbestos (*Hofmann*, 1869). Other oxidizing agents lead directly to formic acid.

It is a gas, condensible by cold to a clear mobile liquid, which boils at −21°. A solution of about 40 per cent. is an

article of trade. In solution it has apparently the hydrate-formula, $C(H_2)(OH)_2$. (Cf. Chem. Ztg. for 1890, p. 1408.)

It polymerizes very readily, yielding, according to the conditions of the experiment:

(1) **Para-formic aldehyde**, probably $(CH_2O)_2$, a white mass soluble in water; or

(2) **Trioxy-methylene**, probably $(CH_2O)_3$, a crystalline compound which passes into formic aldehyde again on being volatilized; or

(3) **Formose** (which see), a mixture of several compounds of the nature of glucose. On account of this facility for undergoing polymerization, formic aldehyde in all probability plays an important part in assimilation by plants.

By its combination with hydrochloric acid, **Chloro-methyl alcohol** (*Chloro-methanol*), $CH_2Cl(OH)$, and **Oxy-chloro-methyl ether** (*Chloro-methane-oxy-methanol*), $CH_2Cl—O—CH_2OH$, result. Both of these are colourless liquids, which react in many respects like formic aldehyde itself.

Methylal, $CH_2(OCH_3)_2$ (see p. 143), is frequently made use of instead of formic aldehyde, for carrying out condensation reactions. It is employed in medicine as a soporific, and is also used as an extractive for certain scents. B. Pt. 42°.

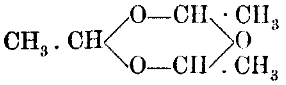
Acetic Aldehyde (*Ethanal*), *Aldehyde*, $CH_3—CHO$, was formerly termed "acetyl hydride," $C_2H_3O.H$ (*Fourcroy* and *Vauquelin*, 1800; composition established by *Liebig* in 1835; name taken from "alcohol dehydrogenatus"). It is prepared by passing ammonia gas into an ethereal solution of the crude aldehyde, obtained by oxidizing alcohol with $K_2Cr_2O_7 + H_2SO_4$ and drying over $CaCl_2$, washing the precipitated aldehyde-ammonia with ether, and finally distilling it with dilute sulphuric acid. It is obtained in large quantity as a by-product in the first portions of the distillate in the manufacture of spirit. For its production in place of vinyl alcohol, $C_2H_3.OH$, from acetylene, see p. 63.

Colourless mobile liquid, B. Pt. 21°; Sp. Gr. about 0·8. Has a peculiar aromatic and suffocating odour, producing a kind of cramp in the chest when inhaled. Burns with a luminous flame and dissolves sulphur, phosphorus, and iodine. Is readily soluble in water, alcohol, and ether. Chlorine converts it into acetyl chloride.

Para-aldehyde, $C_6H_{12}O_3$, is a liquid difficultly soluble in water. M. Pt. + 10°; B. Pt. 124°, *i.e.* more than 100° above that of aldehyde. Is used as a soporific.

Meta-aldehyde, $(C_2H_4O)_x$, crystallizes in white prisms insoluble in water, which sublime at a little over 100°, with partial reconversion into aldehyde. (See B. **14**, 2271).

Meta-aldehyde is changed back again into ordinary aldehyde by prolonged heating to 115° in sealed tubes, and also, as is the case with para-aldehyde, by distillation with somewhat dilute sulphuric acid. Para-aldehyde reacts in the same way as ordinary aldehyde with PCl_5, but not with NH_3, $NaHSO_3$, $AgNO_3$, and NH_2OH. The constitution of para-aldehyde may be taken as:



(*Kekulé* and *Zincke*).

(The connection of 3 molecules of aldehyde by C-bonds cannot be assumed, on account of the readiness with which para-aldehyde breaks up into the former.)

With regard to these and other polymeric compounds, the general rule has been proved to hold, that in the case of bodies of similar constitution, the one of simpler composition is the more soluble, possesses the lower melting point, and is the more easily vaporized.

Acetal, $C_2H_4(OC_2H_5)_2$. B. Pt. 104°. This, as well as methylal, is frequently used instead of aldehyde for the carrying out of condensation reactions (see p. 144).

Aldehyde-ammonia (1-*Ethanol-amine*), $CH_3—CH(OH)(NH_2)$. Cf. pp. 143 and 147. This may be used for the preparation of hydrazine, $H_2N—NH_2$ (cf. *Curtius* and *Jay*, B. **23**, 740).

Propylic aldehyde, $C_2H_5.CHO$, is present in wood tar. Normal **Heptylic aldehyde** (*Oenanthol*), $C_7H_{14}O$, is obtained by the dry distillation of castor oil under diminished pressure, etc.

The **normal aldehydes**, C_{12}, C_{14}, C_{16} and C_{18} are also known.

Mono- and Di-chlor-aldehyde, CH_2ClCHO, and $CHCl_2CHO$, are liquids boiling respectively at 85° and 89°.

Chloral,* $CCl_3.CHO$, (*Liebig*), is a liquid which boils at 98°, and which—when impure—easily changes into a solid polymeric modification, meta-chloral, but is regenerated from this upon heating. It combines readily with water to **chloral hydrate** $CCl_3.CH(OH)_2$, (see p. 143, *b*), and with alcohol to **Chloral alcoholate**, $CCl_3{-}CH(OH)(OC_2H_5)$, and **Tri-chloro-acetal**, $CCl_3{-}CH(O.C_2H_5)_2$. The end product of the action of chlorine upon alcohol consists chiefly of the last three substances, which are converted into chloral by distilling with sulphuric acid, and rectifying over lime.

Chloral is an oily liquid of a sharp and characteristic odour. It combines with sodium bisulphite, ammonia, hydrocyanic acid and acetic anhydride, and reduces an ammoniacal solution of silver. It is easily oxidized to tri-chloracetic acid, and broken up by alkali into chloroform and alkaline formate:

$$CCl_3CH.O + HKO = CCl_3H + HCO_2K.$$

Chloral Hydrate, $CCl_3.CH(OH)_2$, forms crystals readily soluble in water, melting at 57°, and boiling with dissociation at 97°. It acts as a soporific and antiseptic. Sulphuric acid converts it into chloral. **Chloral alcoholate** and **Trichloro-acetal** (see above) both form colourless crystals.

Of the aldehydes poorer in hydrogen must be mentioned, in addition to **Crotonic aldehyde** (p. 145),

Acrolein,† *Acrylic aldehyde, Allyl aldehyde*, $CH_2{=}CH{-}CHO$, which is produced by the oxidation of allyl alcohol, by the distillation of fats, and by heating glycerine with bisulphate of potash. It is a liquid boiling at 52°, of pungent odour (the smell of burning fat being due to it), and of violent action

* "O.N." 2-Trichloro-ethanal. † "O.N." Propenal.

upon the mucous membrane of the eyes. It unites in itself the properties of an aldehyde and of a compound poorer in hydrogen, and therefore combines with ammonia and with bromine; it also unites with hydrobromic acid to *Bromo-propionic aldehyde*, $CH_2Br—CH_2—CHO$.

Acrolein-ammonia yields picoline, C_6H_7N, upon distillation (see Pyridine bases), and crotonic aldehyde-ammonia, by an analogous reaction, collidine, $C_8H_{11}N$.

Acrolein is capable of combining with two atoms of bromine to Di-bromo-acrolein (di-bromo-propyl aldehyde), $CH_2Br—CHBr—CHO$, a compound which is of importance in the synthesis of the sugars. (See p. 307.)

Crotonic aldehyde, $C_3H_5—CHO$, is obtained by the action of zinc chloride or, better, sodium acetate (B. **25**, R. 732) upon aldehyde (see p. 145), and also by the distillation of aldol. It is a colourless liquid of suffocating odour; B. Pt. 104°.

Aldoximes.

Aldoxime (*Ethane-oxime*), $CH_3—CH{=}N—OH$, is prepared from an aqueous solution of aldehyde and hydroxylamine hydrochloride, with the addition of soda; it boils at 115° without decomposition.

The *Constitution of the Aldoximes* is arrived at from the following reactions (see also p. 145):—

1. They yield primary amines upon reduction (p. 123; B. **19**, 3232; **20**, 728).

2. By virtue of the "hydroxyl" hydrogen of the "oxime" group ($=N—OH$), they are capable of forming alkyl derivatives (ethers) and acid derivatives (esters). The alkyl compounds are broken up by hydrochloric acid into aldehyde and alkyl-hydroxylamine (see p. 128); the hydroxyl of the oximes is therefore linked to the nitrogen.

3. The aldoximes are split up by acetic anhydride (all of them, at least, upon being warmed) into nitrile and water:

$$CH_3—CH{=}NOH = CH_3.CN + H_2O.$$

4. The oximes of the fatty series readily take on HCN to the group $=C{=}N—$, forming the group $=C\langle{}^{NH.OH}_{CN}$, just as in the case of the aldehydic group $=C{=}O$ (p. 144).

The aldoximes are structural isomers of the amides, into

which they can pass by an interesting molecular transformation (*Beckmann*). Many of the aldoximes exist in *two isomeric modifications*, which can be readily converted, the one into the other, and which are *structurally identical* (*H. Goldschmidt*); this isomerism rests upon *stereo-chemical grounds*. For further details see the Ketoximes (p. 158), which are in every respect analogous.

B. Ketones.

The lowest member of the series, Acetone, contains three atoms of carbon. The higher members, from C_{12} on, are solid. They are all lighter than water, *e.g.*, the Sp. Gr. of acetone is 0·81 at 0°.

Occurrence. Acetone is present in urine, methyl-nonyl ketone in oil of rue, Ruta graveolens.

Modes of formation. 1. By the oxidation of secondary alcohols, which lose thereby two atoms of hydrogen:

$$\underbrace{CH_3.CH(OH).CH_3}_{\text{Iso-propyl alcohol.}} + O = \underbrace{CH_3.CO.CH_3}_{\text{Acetone.}} + H_2O.$$

Many other compounds also, which contain secondary hydrocarbon radicles, yield ketones upon oxidation, *e.g.* iso-butyric acid.

2. From acids by the dry distillation of their calcium or barium salts, carbon dioxide being formed:

$$2CH_3—COOca = \begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CO + CO_3Ca.$$

In the case of the higher molecular fatty acids, this reaction can be brought about by heating with phosphoric anhydride (B. **23**, Ref. 502).

When two different acids are employed, mixed ketones, *i.e.* ketones containing different alcohol radicles, result, thus:

$$\underbrace{CH_3—COOca + CH_3.CH_2.COOca}_{\text{Calcium acetate and propionate.}} = \underbrace{\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>\!CO}_{\text{Methyl-ethyl ketone.}} + CO_3Ca.$$

From an acid C_n there is thus formed a ketone C_{2n-1}, from two acids C_n and C_m a ketone C_{n+m-1}. When formate of calcium is used, formic aldehyde results.

3. From di-chlorides containing the atomic group $=CCl_2$:

$$\underbrace{(CH_3)_2CCl_2}_{\text{Acetone chloride.}} + H_2O = \underbrace{(CH_3)_2CO}_{\text{Acetone.}} + 2HCl.$$

One might expect here that two chlorine atoms would be exchanged for two hydroxyls, and a compound of alcoholic character, a diatomic alcohol, acetonyl-glycol, $(CH_3)_2C{=}(OH)_2$, would be formed. But the law, already mentioned under aldehyde, that several hydroxyls cannot as a rule exist beside one another joined to the same carbon atom, is further exemplified in this instance also. Derivatives of such a glycol are, however, capable of existence.

4. By the action of zinc-alkyl upon an acid chloride, *e.g.* acetyl chloride, $CH_3.COCl$:

$$CH_3.COCl + CH_3zn = {CH_3 \atop CH_3}{>}CO + Clzn. \quad (zn = \tfrac{1}{2}\,Zn.)$$

An addition compound is first formed, which must be quickly decomposed by water, otherwise tertiary alcohols are produced. This method of formation, which was devised by *Freund* in 1861, allows of the preparation of any possible ketone by using the corresponding zinc-alkyl and acid chloride, *e.g.*:

$$\underbrace{C_3H_7.CO.Cl}_{\text{Butyric chloride.}} + C_2H_5zn = \underbrace{C_3H_7.CO.C_2H_5}_{\text{Ethyl-propyl ketone.}} + Clzn.$$

At the same time it elucidates, together with method 2, the *constitution* of the ketones, from the constitution of the corresponding acids. Theoretically, therefore, ketones are compounds which contain the carbonyl group, CO, linked on both sides with an alcohol radicle, R—CO—R. If the alcohol radicles are the same, "simple" ketones result, and if different, "mixed" ketones.

The ketones may also be regarded as derived from monobasic acids by the exchange of their hydroxyl for alkyl, corresponding with modes of formation 2 and 4, and also from aldehydes by exchange of hydrogen for alkyl.

The existence of ketones with less than 3 atoms of carbon is theoretically impossible.

5. From the ketonic acids or their ethers, *e.g.* aceto-acetic ether, $CH_3—CO—CH_2—CO.OC_2H_5$, by warming with moderately dilute sulphuric acid or with dilute alkalies. This important reaction will be treated of at greater length under aceto-acetic ether.

6. From the hydrocarbons of the acetylene series (see p. 63), by the action of mercuric salts and also of dilute sulphuric acid.

7. Acetone and some of its homologues result from the dry distillation of wood, and are therefore present in crude wood naphtha.

Isomers. The ketones show among themselves the same isomerism as the secondary alcohols. This isomerism depends on the one hand upon the isomerism of the alcohol radicles which are linked together by the CO-group, (different carbon atom chains), and on the other by the position of the oxygen atom on similar carbon chains, (isomerism of position); thus, $C_4H_9—CO—CH_3$ is isomeric with $C_3H_7—CO—C_2H_5$.

The aldehydes containing an equal number of carbon atoms in the molecule are always isomeric with the ketones, since both classes of compounds are formed from isomeric alcohols by the separation of H_2.

This kind of isomerism may also be compared with metamerism, *e.g.* with that of methyl-butyl ether and ethyl-propyl ether.

Further, acetone is isomeric with allyl alcohol. Such an isomerism of a saturated with an unsaturated compound is termed "saturation isomerism" (cf. p. 37).

Nomenclature. After the name of the alcohol radicle the syllable "ketone" is appended, *e.g.* di-ethyl kètone, $(C_2H_5)_2CO$, and methyl-ethyl ketone, $CH_3—CO—C_2H_5$. Acetone is consequently di-methyl ketone. The names of the simple ketones are also derived from the acids which yield them, *e.g.* "Valerone," $(C_4H_9)_2CO$, from valeric acid.

Baeyer (B. 19, 160) terms the ketones *Keto-substitution products* of the hydrocarbons, *e.g.* acetone is keto-propane, and ethyl-methyl ketone is α-keto-butane (the oxygen is attached to the α-carbon atom; see *Substituted fatty acids*).

The "official name" (p. 28) of the ketones ends in "one," *e.g.* Propanone, etc.

Behaviour. 1. The ketones are reducible to secondary alcohols: $(CH_3)_2CO + H_2 = (CH_3)_2CH.OH$.

At the same time pinacones are formed in small quantity, (see p. 86), these going into the pinacolines (pp. 157 and 207) corresponding to the ketones, when warmed with acids.

2. Oxidizing agents, *e.g.* $K_2Cr_2O_7$ and dilute H_2SO_4, slowly convert the ketones into acids containing a lesser number of carbon atoms in the molecule, (not—as in the case of the aldehydes—into acids containing an equal number), the carbon chain being broken:

$$CH_3—CO.CH_3 + O_4 = CH_3.COOH + CO_2 + H_2O.$$

Since carbon is tetravalent, the CO group in the ketone, being already linked to two alcohol radicles, can only pass into the group COOH, which characterizes the acids (p. 166), if one of the alcohol radicles be split off. For the laws which govern the course of these oxidations, see B. **25**, R. 121.

Since the acids formed by oxidation bear no reciprocal relation to the ketone, and the oxidation process is more complicated than in the case of the aldehydes, it is easy to understand why the ketones do not possess reducing properties.

3. Phosphorus pentachloride, PCl_5, converts the ketones into the corresponding dichlorides, acetone, for instance, into acetone chloride, $(CH_3)_2CCl_2$.

4. Addition-reactions. (*a*) The ketones do not as a rule combine with water and alcohol, for the reasons given under the aldehydes and at p. 152.

They form with mercaptan "mercaptols," analogous to acetal, *e.g.* $(CH_3)_2C(SC_2H_5)_2$. (B. **18**, 883.)

(*b*) With ammonia there result the (basic) acetone-amines, with separation of water, *e.g.* di-acetone-amine, $C_6H_{13}NO$, tri-acetone-amine, $C_9H_{17}NO$, (*Heintz*); this reaction is more complicated than that with the aldehydes, two or three molecules of acetone combining with one molecule of ammonia, with elimination of water.

(*c*) The ketones which contain the group $CH_3—CO—$, and also some others, combine with acid sodium sulphite to crystalline compounds, *e.g.* acetone to $(CH_3)_2C{<}^{OH}_{SO_3Na} + H_2O$, (glancing mother-of-pearl plates); these go back into ketones,

for the most part, when treated with soda solution. This very important reaction is made use of in separating and purifying the ketones.

(*d*) With hydrocyanic acid are formed the nitriles of higher acids, as in the case of the aldehydes; *e.g.* $(CH_3)_2C<^{OH}_{CN}$.

5. The ketones, unlike the aldehydes, do not possess the property of polymerizing, but they form condensation products. Just as aldehyde is converted into crotonic aldehyde, so is acetone, by the action of many reagents—*e.g.* CaO, KOH, HCl, and H_2SO_4—converted with elimination of water, into mesityl oxide, $C_6H_{10}O$, phorone, $C_9H_{14}O$, or mesitylene, C_9H_{12}, according to the conditions, (see benzene derivatives):

$$2C_3H_6O = C_6H_{10}O + H_2O.$$
$$3C_3H_6O = C_9H_{14}O + 2H_2O.$$
$$3C_3H_6O = C_9H_{12} + 3H_2O.$$

Analogous condensations also ensue with other ketones or aldehydes under the influence of dilute caustic soda or of sodium ethylate, (B. **20**, 655). In this way the more complicated ketones result, (A. **218**, 121).

6. Sulphuretted hydrogen converts the ketones into thio-compounds, *e.g.* acetone into thio-acetone, $CH_3—CS—CH_3$, (B. **16**, 1368).

7. Halogens give rise to substitution products.

8. Like the aldehydes, the ketones—even C_{35}—combine with hydroxylamine to oximes, which are termed *Acetoximes* or *Ketoximes.* (*V. Meyer*, B. **15**, 1324, 2778; **16**, 823, 1784, etc.) Thus:

$$(CH_3)_2CO + NH_2OH = H_2O + \underbrace{(CH_3)_2C{=}N.OH.}_{\text{Acetoxime.}}$$

These are for the most part solid, readily volatile compounds which react in a manner exactly analogous to the aldoximes (p. 150), and which therefore possess a similar constitution. For further particulars, see p. 158.

9. Analogous reactions follow with the hydrazines, *e.g.*

phenyl-hydrazine, $C_6H_5—NH—NH_2$ (*E. Fischer*, B. 17, 572), with the formation of "hydrazones" (p. 146).

$$(CH_3)_2CO + H_2N—NH—C_6H_5$$
$$= \underbrace{(CH_3)_2C{=}N—NH—C_6H_5}_{\text{Acetone-phenyl-hydrazone.}} + H_2O.$$

Phenyl-hydrazine and hydroxylamine are therefore of great value for the recognition of the aldehydic or ketonic character of a substance.

10. Nitrous acid (nitrous ether and sodium ethylate) gives rise to **Iso-nitroso-ketones**, *e.g.* iso-nitroso-acetone, $CH_3—CO—CH—N.OH$, by the separation of H_2O and the replacement of H_2 by the group $=N.OH$ (oxime). These are converted by reduction into **Amido-ketones**, *e.g.* amido-acetone, $CH_3—CO—CH_2.NH_2$, unstable basic compounds which readily give up water and change into ketines (p. 530). The oxime group in the iso-nitroso-ketones can be replaced by an atom of oxygen, whereby ketone-aldehydes or di-ketones (p. 238) are produced.

Acetone (2-*Propanone*), C_3H_6O, $= CH_3—CO—CH_3$.

Acetone has been known for a long time; its formula was established by *Liebig* and *Dumas* in 1832.

It is present in very small quantity in normal urine, in the blood, in serum, etc., but in much larger quantity in pathological cases such as acetonuria and diabetes mellitus. It is produced, among other ways, by the distillation of sugar, gum, cellulose, etc., and is therefore present in wood spirit; also by acting upon allylene, C_3H_4, with $HgCl_2$ (p. 63). On the large scale it is prepared by the dry distillation of acetate of lime.

Properties. (See under general behaviour of the ketones.) Liquid of peculiar ethereal and refreshing odour; B. Pt. 56°; Sp. Gr. 0·81 at 0°. Soluble in water, and separated from the aqueous solution on addition of salts. Miscible also with alcohol and ether. $KMnO_4$ does not oxidize it in the cold, but CrO_3 does, with formation of acetic and carbonic acids. Shows the aldehydic reaction with fuchsine and sulphurous acid.

Detection of acetone, *e.g.* by the formation of indigo when it acts upon o-nitro-benz-aldehyde in presence of a little caustic soda solution.

Chloro-acetone, *metacyl chloride*, $CH_3—CO—CH_2Cl$, is a liquid which produces a copious flow of tears. B. Pt. 119°.

Per-bromo-acetone, $CBr_3—CO—CBr_3$, is also known. (See p. 336.)

Cyano-acetone (2-*Butanone-4-Nitrile*), $CH_3—CO—CH_2—CN$, is a colourless liquid which polymerizes very readily. It yields a sodium compound.

Iso-nitroso-acetone, $CH_3—CO—CH=N.OH$ (B. **15**, 3067), is formed by the action of nitrous acid upon acetone or aceto-acetic ether; M. Pt. 65°.

Amido-acetone, $CH_3—CO—CH_2.NH_2$. A basic compound, which readily loses water and passes into dimethyl-pyrazine.

Sulphonal, $(CH_3)_2—C(SO_2.C_2H_5)_2$, is formed when a mixture of acetone and mercaptan is treated with hydrochloric acid, and the **Mercaptol**, $(CH_3)_2C(SC_2H_5)_2$ [a derivative of the hypothetical acetone-glycol, $(CH_3)_2C(OH)_2$], which is thus formed, is oxidized by potassium permanganate to the corresponding sulphone. Prisms, M. Pt. 125°; acts as a soporific.

Mesityl oxide, $C_6H_{10}O$, = $CH_3—CO—CH=C(CH_3)_2$ (*Kane*, 1838; *Baeyer*), is a liquid of aromatic odour, boiling at 132°.

Phorone, $C_9H_{14}O$, = $CH_3—CO—CH=C(CH_3)[CH=C(CH_3)_2]$, forms yellow crystals which melt easily. Both of these compounds are obtained by saturating acetone with hydrochloric acid gas (A. **180**, 1).

Methyl-ethyl ketone (2-*Butanone*), $CH_3—CO—C_2H_5$, is present in crude wood spirit, and also results from the oxidation of secondary butyl alcohol. B. Pt. 81°.

Isonitroso-methyl-acetone (2-*Butanone-3-oxime*), $CH_3-CO-C(N.OH)-CH_3$. From methyl-aceto-acetic ether and nitrous acid (B. **20**, 531). For its conversion into di-acetyl, see **p. 238.**

Di-ethyl ketone (3-*Pentanone*), *propione*, $(C_2H_5)_2CO$. M. Pt. 104°.

Di-propyl ketone (4-*Heptanone*), *butyrone*, $(C_3H_7)_2CO$. M. Pt. 144°.

Pinacoline (2-*Dimethyl-3-Butanone*), *methyl-tertiary-butyl ketone*, $CH_3—CO—C\equiv(CH_3)_3$, results by a peculiar molecular transformation, the "pinacoline reaction," from the action of dilute sulphuric acid upon pinacone. (See p. 207.) B. Pt. 106°.

Methyl N.-nonyl ketone, $CH_3—CO—C_9H_{19}$, is the chief constituent of oil of rue (from Ruta graveolens). B. Pt. 225°.

Ketones with 11, 12, 13, 14, 15, 16, 17, 18 and 19 carbon atoms are also known; further,

Laurone, $C_{23}H_{46}O$, from calcium laurate.

Myristone, $C_{27}H_{54}O$, from calcium myristate.

Palmitone, $C_{31}H_{62}O$, from calcium palmitate.

Stearone, $C_{35}H_{70}O$, from calcium stearate; and, finally, the ketones, C_{20},

C_{22} and C_{24}, which are obtained by distilling the normal heptylate with myristate, palmitate, or stearate of lime.

All these ketones have been converted by *Krafft* into the corresponding paraffins, by first transforming them into the chlorides, $C_nH_{2n}Cl_2$, by means of PCl_5, and then heating the latter with hydriodic acid and phosphorus.

Ketoximes.

Acetoxime (*2-Propane-oxime*), $(CH_3)_2C=N.OH$, forms crystals which are readily soluble in water, alcohol and ether; these melt at 65°, and volatilize without decomposition at 135°.

Stereo-isomeric oximes. Like the aldoximes (p. 150), many of the ketoximes show cases of structural isomerism, this depending upon the configuration of the molecule, *i.e.* upon the position of the hydroxyl which is linked to the nitrogen (see Nitrogen-isomerism, p. 25). These isomers, which can be transformed one into the other, show certain chemical differences, the latter being manifestly conditioned by the spacial proximity of the reacting groups. The one variety of *aldoximes* —as opposed to the other—gives up water even in the cold, when acted upon by acetic anhydride, and passes into a nitrile, from which the conclusion is drawn that the hydroxyl and aldehydic hydrogen are spacially near to one another (the "syn" position, *i.e.* syn-aldoximes, in contradistinction to the "anti" position, *i.e.* anti-aldoximes). (See figs. I. and II.):—

```
(I.) R—C—H        (II.) R—C—H       (III.) R—C—R′
       ||                 ||                 ||
       N—OH           HO—N                   N—OH
```

"Syn"-Aldoximes.	"Anti"-Aldoximes.	Ketoximes.

In the case of the *Ketoximes* an analogous difference exists when they are asymmetric (*i.e.* R different from R′), since they show a different behaviour in the "*Beckmann* molecular transformation" (see Tolyl-phenyl-ketoxime), according as they belong to the "syn" or to the "anti" series (see B. **24,** 23; *Beckmann*, B. **22,** 431; *Hantzsch* and *Werner*, B. **23,** 1; B. **24,** 13, 3479, 4018; **25,** 1908, 2164).

COMPARISON OF THE ALDEHYDES AND KETONES.

ALDEHYDES, X . CHO.	KETONES, $\genfrac{}{}{0pt}{}{X}{X}{>}CO$.
Modes of formation.	**Modes of formation.**
1. By the oxidation of primary alcohols, C_n* (and other substances).	1. By the oxidation of secondary alcohols, C_n (and other compounds).
2. By the reduction of acids, C_n. (Distillation of the Ca salts with calcium formate).	2. From acids by distillation of their mixed calcium salts.
3. From the di-chlorides, X . $CHCl_2$.	3. From di-chlorides, $\genfrac{}{}{0pt}{}{X}{X}{>}CCl_2$.
——	4. From acid chlorides and zinc alkyl.
——	5. From ketonic acids, with separation of CO_2.
Properties.	**Properties.**
1. Reducible to primary alcohols.	1. Reducible to secondary alcohols.
2. Oxidizable to acids, C_n; strongly reducing.	2. Oxidizable to acids, C_{n-x}; not reducing.
3. Yield with PCl_5 di-chlorides, $-CHCl_2$.	3. Yield with PCl_5 dichlorides, $>CCl_2$.
4. Capable of combining with [(*a*) water; (*b*) alcohol, acetic acid (seldom)]; (*c*) ammonia; (*d*) sodium bisulphite, to crystalline compounds; (*e*) hydrocyanic acid, to nitriles of higher acids.	4. Capable of combining with [(*a*) water; (*b*) alcohol, both seldom], (*c*) ammonia, to acetone-amines with separation of water; (*d*) sodium bisulphite, to crystalline compounds; (*e*) hydrocyanic acid, to nitriles of higher acids.
5. Capable of polymerization, often with production of resin when KOH is used.	5. ——
6. Condensible, *e.g.* to aldol, $C_4H_8O_2$, and to crotonic aldehyde.	6. Condensible, *e.g.* to $C_6H_{10}O$, $C_9H_{14}O$, C_9H_{12}.
7. Capable of substitution, *e.g.* to chloral, $CCl_3 . CHO$.	7. Capable of substitution, *e.g.* to chloro-acetone, $CH_3-CO-CH_2Cl$.
8. Yield with H_2S, *thio-aldehydes*.	8. Yield with H_2S, *thio-acetones*.
9. Yield with hydroxylamine, oximes, $-CH=N . OH$.	9. Yield with hydroxylamine, ketoximes, $>C=N . OH$.
10. Yield with hydrazines, hydrazones.	10. Yield with hydrazines, hydrazones.

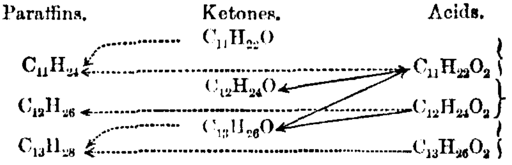
* n means an equal number of carbon atoms.

The proof, furnished by *Krafft*, that (what are termed) the "normal" paraffins, etc., contain a *straight carbon-atom chain*, rests upon the possibility of preparing the ketones C_{n+1} from the acids C_n, by distilling their barium salts with barium acetate, without any branching of the carbon chain (since the carboxyl of the acid occupies an end-position, and consequently also the methyl group which replaces the hydroxyl); the oxidation of those ketones into the acids C_{n-1}; and, lastly, the conversion of these three compounds into the corresponding paraffins C_n, C_{n+1} and C_{n-1}.

Paraffins which contain the same number of carbon atoms in the molecule are proved to be identical, even though they may be derived from different sources.

The paraffin C_{n-1} results from the acid C_{n-2}, according to the above reaction. If, therefore, the acid C_{n-2} is normal, so are also the paraffin C_{n-1}, the acid C_n, and so on. The question of the constitution of any paraffin is thus referable to that of one which contains two atoms of carbon less in the molecule (or its corresponding acid). If we follow those relations downwards, beginning with the acids C_{18}, C_{16}, C_{14} and C_{12} which occur in nature (see these), we arrive finally at nonylic acid, which is undoubtedly normal from its synthesis; consequently those acids and their derived paraffins, ketones, etc., are also normal.

We have, for instance, the following relations:



Cf. the Aldehydes and Ketones on p. 159.

VI. MONOBASIC FATTY ACIDS.

A. Saturated Acids, $C_nH_{2n}O_2$. (See Table, p. 161.)

By the oxidation of the primary alcohols or of their corresponding aldehydes the monobasic fatty acids are formed, the saturated alcohols yielding the saturated monobasic fatty acids, or "acids of the aliphatic series" as they are termed, corresponding to which, as to the alcohols, there are unsaturated compounds. These acids are monobasic, *i.e.* contain in the molecule only one replaceable atom of hydrogen, because they give rise to only one series of salts or of ethers. They are known as the *fatty* acids, on account of many of them being either contained in fats or resulting from these by oxidation.

The lower members of the series are liquids of pungent odour and corrosive action which boil without decomposition,

SUMMARY OF THE ACIDS, $C_nH_{2n}O_2$.

		M. Pt.	B. Pt.			M. Pt.	B. Pt.
Formic acid . .	CH_2O_2	9°	99°	Undecylic acid .	$C_{11}H_{22}O_2$	28°	213°
Acetic ,, . .	$C_2H_4O_2$	17°	118°	Lauric ,, .	$C_{12}H_{24}O_2$	43°	226°
Propionic ,, . .	$C_3H_6O_2$	Liquid.	141°	Tridecylic ,, .	$C_{13}H_{26}O_2$	40°	236°
Butyric ,, normal	$C_4H_8O_2$	0°	163°	Myristic ,, .	$C_{14}H_{28}O_2$	54°	248°
Butyric ,, iso- .	$C_4H_8O_2$	Liquid.	154°	Penta-decylic ,, .	$C_{15}H_{30}O_2$	51°	257°
Valeric ,,				Palmitic ,, .	$C_{16}H_{32}O_2$	62°	269°
1. Normal . .	$C_5H_{10}O_2$	Liquid.	186°	Margaric ,, .	$C_{17}H_{34}O_2$	60°	277°
2. Common or iso- .	$C_5H_{10}O_2$	Liquid.	175°	Stearic ,, .	$C_{18}H_{36}O_2$	69°	287°
3. Tri-methyl-acetic	$C_5H_{10}O_2$	35°	164°	Nondecylic ,, .	$C_{19}H_{38}O_2$	66°	298°
4. Methyl-ethyl-acetic	$C_5H_{10}O_2$	Liquid.	175°	Arachidic ,, .	$C_{20}H_{40}O_2$	77°	
Caproic acid	$C_6H_{12}O_2$	-2°	205°	Behenic ,, .	$C_{22}H_{44}O_2$	76°	
Heptoic ,, †	$C_7H_{14}O_2$	-10°	224°	Lignoceric ,, .	$C_{24}H_{48}O_2$	80°	
Caprylic ,, †	$C_8H_{16}O_2$	+16°	236°	Cerotic ,, .	$C_{27}H_{54}O_2$	78°	
Nonylic ,, †	$C_9H_{18}O_2$	12°	254°	Melissic ,, .	$C_{30}H_{60}O_2$	90°	
Capric ,,	$C_{10}H_{20}O_2$	30°	269° / 202°*				

* M. Pt. under 100 m.m. pressure. From C_6 onwards, the boiling points given are those of the normal compounds.

† These are also termed heptoxylic-, octoxylic-, nonoxylic acids, etc.

dissolve readily in water, and show a strongly acid reaction. The middle members have an unpleasant smell like that of rancid butter or perspiration, and are oily and but slightly soluble in water. Mobility, odour and solubility diminish with increasing carbon. The higher members, from C_{10} on, are solid, like paraffin, and insoluble in water, and can only be distilled without decomposition in a vacuum. Their acid character no longer finds expression in their reaction, but in their capability of forming salts with bases. They remain easily soluble in alcohol and especially in ether.

For the laws governing the melting and boiling points, see pp. 35 and 33. The Sp. Gr. of the liquid acids is at first > 1, and from C_3 onwards < 1, and it decreases continuously down to about 0·8, the paraffin character of the hydrocarbon radicle becoming preponderant.

Occurrence. Many of the acids of this series are found in nature in the free state, but more frequently as ethers, viz. :— (*a*) ethers of monatomic alcohols (see wax varieties), (*b*) ethers of glycerine or glycerides, in most of the vegetable and animal fats and oils. For further particulars see p. 176.

Formation. 1. By the oxidation of the primary alcohols, $C_nH_{2n+1}OH$, or their aldehydes, $C_nH_{2n}O$, by means of $K_2Cr_2O_7$ or MnO_2 and dilute H_2SO_4, or by the oxygen of the air in presence of platinum or of nitrogenous substances, *e.g.* acetic acid from alcohol.

1ª. Acids containing less carbon are formed by the oxidation of many other compounds, such as ketones, secondary and tertiary alcohols, etc., with separation of carbon. The higher molecular acids of this series are likewise converted into their lower homologues upon oxidation.

2. Several acids have been prepared from the halogen compounds $C_nH_{2n-1}X_3$, which contain the group $-CX_3$, *e.g.* :

$$HCCl_3 + 4KOH = H.CO_2K + 3KCl + 2H_2O.$$

From this mode of preparation one might expect an exchange of the three chlorine atoms for three hydroxyls, with formation of the intermediate compounds $H . C{\equiv}(OH)_3$ or $R—C(OH)_3$. Such compounds are however incapable of existence for the reasons stated under the aldehydes and ketones, going over into acids with elimination of water, thus :

$$R—C(OH)_3 = R—CO.OH + H_2O.$$

But derivatives of these (which may be regarded as triatomic alcohols and termed "ortho-acids,") are known, *e.g.* **ortho-formic ethyl ether,** $HC(OC_2H_5)_3$, a neutral liquid of aromatic odour, insoluble in water, and boiling at 146°.

3. From the cyanogen compounds of the alcohol radicles, $C_nH_{2n+1}CN$. The cyanides, *i.e.* nitriles, which are prepared by warming the iodides of the alcohol radicles with cyanide of potassium, are converted into the fatty acids and ammonia by saponification, *e.g.* by heating with potash, with dilute or concentrated hydrochloric acid, or with sulphuric acid diluted with its own volume of water, thus:

$$CH_3.CN + 2H_2O = CH_3.CO_2H + NH_3.$$

In this way hydrocyanic acid yields formic acid and ammonia, and it may therefore be regarded as the nitrile of the former. Amides are formed as intermediate products. (See pp. 118 and 194.)

The great importance of this reaction, by means of which we can obtain an acid C_{n+1} from an alcohol C_n, has been already indicated, (p. 118). And since the acids, albeit with some difficulty, can be converted by reduction into the corresponding alcohols, it is thus possible to build up synthetically, step by step, the alcohols richer in carbon from those poorer in carbon, a circumstance which is of especial importance in the case of the normal alcohols. (*Lieben* and *Rossi*, see p. 86.)

4. The acids may be regarded as resulting from the paraffins $C_{n-1}H_{2(n-1)+2}$ and CO_2, *e.g.* acetic acid from CH_4 and CO_2, and formic acid from H_2 and CO_2. These two components can in fact be made to combine indirectly, thus carbonic acid unites with potassium or sodium alkyl upon warming (*Wanklyn*):

$$CH_3Na + CO_2 = CH_3.CO_2Na.$$

Formic acid is obtained in an analogous manner from nascent hydrogen and carbon dioxide, under the influence of the silent electric discharge:

$$H_2 + CO_2 = H.CO_2H;$$

or from hydrogen, potassium and carbon dioxide, when the potassium is placed in a bell-jar filled with moist carbonic acid (*Kolbe* and *Schmitt*, 1861); or by treating carbonate of ammonia, etc., with sodium amalgam. Propionic acid is formed by the action of liquid carbon dioxide upon zinc ethide under pressure at 160°.

5. By passing carbonic oxide over heated caustic alkali or alcoholate, thus:

$$CH_3.ONa + CO = CH_3.CO_2Na \text{ (at } 160^\circ\text{)}.$$
$$H.ONa + CO = H.CO_2Na.$$

6. Acid chlorides (p. 190) are produced by the action of phosgene, $COCl_2$, upon zinc alkyl:

$$COCl_2 + znCH_3 = \underbrace{CH_3.COCl}_{\text{Acetyl chloride.}} + znCl;$$

and, on decomposing these with water, the acids themselves are obtained:

$$CH_3.CO.Cl + H_2O = CH_3.CO.OH + HCl.$$

7. From acids poorer in hydrogen by direct or indirect addition of the latter, *e.g.* propionic acid, $C_3H_6O_2$, from acrylic acid, $C_3H_4O_2$. This addition of hydrogen may be effected directly by hydriodic acid and phosphorus, or indirectly, for instance, by addition of hydrobromic acid and backward substitution. Unsaturated acids also yield saturated ones containing fewer carbon atoms when fused with potash, *e.g.* 1 mol. crotonic acid, $C_4H_6O_2$, yields 2 mols. acetic acid, $C_2H_4O_2$.

8. From the oxy-acids, also termed alcoholic acids, by heating them with hydriodic acid:

$$\underbrace{C_3H_6O_3}_{\text{Lactic acid.}} + 2HI = \underbrace{C_3H_6O_2}_{\text{Propionic acid.}} + I_2 + H_2O.$$

9. From many polybasic acids, by the partial separation of CO_2, thus:

$$\underbrace{C_2O_4H_2}_{\text{Oxalic acid.}} = CO_2 + \underbrace{H.CO_2H.}_{\text{Formic acid.}}$$

10. *Aceto-acetic ether syntheses.* The homologues

$$R{-}CH_2{-}COOH \text{ and } {R \atop R'}{>}CH{-}COOH$$

can be prepared from acetic acid by first converting the latter into aceto-acetic ether, $CH_3{-}CO{-}CH_2{-}COO.C_2H_5$, introducing the alcohol radicle into this, and then breaking up backwards the compound so obtained by concentrated alcoholic potash. This reaction will be gone into more fully under aceto-acetic ether (p. 243).

10*a*. An analogous reaction follows on the use of malonic ether (see p. 252).

Separation. Natural fats are nearly all glycerides of several acids, so that a mixture of acids results on their saponification. This mixture may be separated into its components as follows:

(*a*) By fractional distillation in a good vacuum; (*b*) by fractional precipitation of an alcoholic solution of the acids by means of magnesium acetate, calcium chloride, etc., the acids richer in carbon being precipitated first; (*c*) by fractional solution: the dry barium salts of formic, acetic, propionic and butyric acids are very differently soluble in alcohol, the solubility increasing rapidly with increasing carbon; (*d*) by fractional saturation, and distillation of the non-combined acid.

Behaviour. 1. *Salts.* The foregoing acids being monobasic, they form neutral salts, *e.g.* $(C_2H_3O_2)Na$. But they also yield acid salts—the so-called per-acid salts—from the existence of which one might feel inclined to doubt their monobasic nature. These salts are, however, only crystallizable from a strongly acid solution, break up on addition of water, and also lose their excess of acid upon heating. It is therefore permissible to regard them as molecular compounds of the neutral salts with the acids, in which the latter play the part of water of crystallization. All the other chemical characteristics of the acids go to prove their monobasicity.

2. Besides salts, the monobasic acids, simple or substituted, yield other derivatives in a manner exactly analogous to that of the monatomic alcohols. The typical hydrogen atom is replaceable by an alcohol radicle with formation of a compound ether, or by a second acid radicle with formation of an anhydride; the hydroxyl may further be replaced by halogen, especially chlorine, to an acid chloride or chloro-anhydride, by SH to a thio-acid, by NH_2 to an amide, etc. (See Acid derivatives, p. 187.)

3. Halogens act upon the acids as substituents (see p. 182.)

4. Upon heating the alkali salts with soda-lime, or in many cases by heating the silver salt alone, carbonic acid is separated and a paraffin formed, see *e.g.* Methane. Paraffins also result from the electrolysis of the alkaline salts of the acids (see Ethane).

5. Most of the acids are relatively stable towards oxidizing agents, formic acid alone being readily oxidized to carbonic acid, and being therefore a reducing agent.

6. When the lime salts of the acids are heated with calcium formate they are reduced to aldehydes, and when heated for

a lengthened period with hydriodic acid and phosphorus, to paraffins.

6*a*. When the lime salts are distilled alone, or are heated with phosphorus pentoxide, they are transformed into the ketones, $(C_{n-1}H_{2n-1})_2CO$.

7. For their transformation into the amine bases, C_{n-1}, see p. 196.

8. For the "degradation" of the higher acids, see pp. 154 and 196.

Constitution. It follows from their modes of formation, especially 3, 4, and 6, and also from their behaviour (see 3 above), that acetic acid and its higher homologues contain alcohol radicles. The conversion of the alcohols into acids containing one atom of carbon more, by means of the cyanides, is especially strong proof of this. The latter contain the alcoholic radicle bound to the cyanogen group —C≡N, and when they are saponified the alcohol radicle remains unchanged, and the trivalent nitrogen is replaced by O″ and (OH)′, both of these attaching themselves to the carbon atom of the original cyanogen, and so forming the group

$$-CO_2H = -C{\lt}^{O}_{OH}.$$

Consequently all the oxygen in the acid is bound to a single carbon atom in the form of the group CO_2H. This group, which is termed carboxyl, is characteristic of the existence of acid properties. The monobasic acids may therefore be regarded as compounds of the alcohol radicles with carboxyl, thus:

$$C_{n-1}H_{2n-1}.CO_2H = C_nH_{2n}O_2.$$

Formic acid is, in this way, the hydrogen compound of carboxyl, $H.CO_2H$.

The acids are distinguished as *primary*, *secondary*, or *tertiary*, according as the alcohol radicles which they contain are primary, etc.

The monobasic acids may be regarded as being derived from the hypothetical carbonic acid, $CO(OH)_2$, by exchange of hydroxyl for alkyl or hydrogen:

$$CO{\lt}^{C_3H_7}_{OH} = \text{Butyric acid}; \quad CO{\lt}^{H}_{OH} = \text{Formic acid}.$$

They are also termed organic carboxylic acids, and may also

be considered as derived from the paraffins by exchange of an atom of hydrogen for carboxyl. Thus acetic acid is methane-carboxylic acid, etc.

There is no room for doubt that it is the hydrogen atom of the carboxyl group, the so-called "typical" hydrogen atom, which is replaced by metals in the formation of salts, for the foregoing acids are all monobasic, and consequently the number of hydrogen atoms present in the alcohol radicle is of no moment for the acid character. In the di- and polybasic acids, the presence of two or more carboxyls must therefore be assumed.

If one compares the composition of the primary alcohols, $R—CH_2.OH$, with that of the corresponding acids, $R—CO.OH$, (R = alkyl or hydrogen), the latter are seen to be derived from the former by the exchange of two atoms of hydrogen of the carbinol for one atom of oxygen. The character of the original substance is thus completely changed by the entrance of the electro-negative (acidifying) oxygen.

It must not be forgotten that the *constitution* of the aldehydes and ketones, of the primary and secondary alcohols, of glycol, ethylene, ethylene bromide, etc., is deduced from the constitution of the acids.

The rational formulae of the foregoing acids may be written in various ways, according to the reaction which it is desired to indicate. (Cf. p. 26.)

The group $C_2H_3O—$ or $CH_3.CO—$, acetyl (*Ethanoyl*), which together with hydroxyl is common to most of the acetic acid derivatives, and which can be transferred like an element to other compounds by exchange, is termed the *radicle* of acetic acid (see p. 29). The radicles of the homologues are similarly compounded, *e.g.* $H.CO—$, formyl (*Methanoyl*); $C_3H_5O—$, propionyl; C_4H_7O, butyryl, etc. These acid radicles frequently receive the common name "*Acyls*" (*Liebermann*).

The aldehydes may be looked upon as hydrogen compounds of the acid radicles, and the ketones as compounds of the latter with alcohol radicles, thus: $(CH_3.CO)H$ (Aldehyde). $(CH_3.CO)CH_3$ (Acetone).*

Isomers. The acids of the acetic series show the same isomerism as the alcohols containing one atom of carbon less, since they are formed from these by means of the cyanides. Thus there exist one propionic acid, two butyric acids, corre-

* The "official name" (p. 28) of the fatty acids is formed by adding the word "acid" to the name of the paraffin containing an equal number of carbon atoms in the molecule.

sponding to the two propyl alcohols, four valeric acids, corresponding to the four butyl alcohols, and so on. For $C_{10}H_{20}O_2$, 211 isomeric forms are possible. Among all such isomers there is always only one normal acid.

On the other hand, the number of isomeric acids with *n* carbon atoms is always equal to that of the isomeric primary alcohols containing the same number of atoms of carbon.

Formic Acid (*Methanoic acid*), *acidum formicicum*, CH_2O_2 (*Samuel Fisher* and *John Wray*, 1670; *Marggraf*), occurs free in ants, especially Formica rufa, in the processionary caterpillar (Bombyx processionea), in the bristles of the stinging nettle, the fruit of the soap tree (Sapindus saponaria), and in tamarinds and fir cones; also in small quantity in various organic liquids, in perspiration, urine and the juice of flesh.

Formation. From HCN, $CHCl_3$, CH_3OH, CO_2, etc., (see general methods of formation). It also results from the action of sodium amalgam upon ammonium carbonate or alkaline hydrocarbonates, etc.; by the dry distillation or oxidation of many organic substances, *e.g.* starch, (*Scheele*); also by decomposing them—*e.g.* sugar—by concentrated sulphuric acid.

Preparation. 1. Carbonic oxide is readily absorbed by soda-lime at 210°, with formation of sodium formate (*Merz*).

2. When oxalic acid is heated, formic acid is obtained in small quantity together with carbonic oxide, carbonic acid and water, and the same effect is produced by the direct action of sunlight upon its aqueous solution containing uranic oxide:

$$C_2H_2O_4 = CO_2 + CH_2O_2.$$

This decomposition is best effected by heating oxalic acid with glycerine to 100°–110°, (*Berthelot, Lorin*), the formic acid produced combining with the glycerine to an ether, **Monoformin**, (see p. 217):

$$\underbrace{C_3H_5(OH)_3}_{\text{Glycerine.}} + H.CO.OH = \underbrace{C_3H_5{<}{}^{(OH)_2}_{(O.HCO)}}_{\text{Monoformin.}} + H_2O.$$

The monoformin is then saponified either by boiling it with excess of water or by the addition of more oxalic acid, through the water of crystallization of the latter. In this case monoformin and carbon dioxide are again produced, the process repeating itself time after time, a very small amount of glycerine being thus sufficient to convert considerable quantities of oxalic into formic acid. (B. 15, 928.) The anhydrous acid is got by decomposing its lead or copper salt with sulphuretted hydrogen.

Properties. Colourless liquid which solidifies in the cold and fumes slightly in the air. M. Pt. + 9°; B. Pt. 99°; Sp. Gr. 1·22. Has a pungent acid and ant-like odour, acts as a powerful corrosive, and produces sores on the soft parts of the skin. Is stronger than acetic acid and a powerful antiseptic. Decomposes completely into carbonic oxide and water when heated with concentrated sulphuric acid: $CH_2O_2 = CO + H_2O$.

Salts. Potassium-, HCO_2K, Sodium-, HCO_2Na, and Ammonium formate, HCO_2NH_4, form deliquescent crystals. The first two go into oxalates when strongly heated, with evolution of hydrogen (see p. 241); the ammonium salt into formamide and water at 180°:

$$HCO_2.NH_4 = H.CO.NH_2 + H_2O.$$

The lead salt, $Pb(HCO_2)_2$, forms glancing, difficultly soluble needles, the copper salt, $Cu(HCO_2)_2 + 4H_2O$, large blue monoclinic crystals, and the silver salt colourless crystals. The last-mentioned separates silver upon warming, consequently a solution of nitrate of silver is reduced when heated with formic acid.

The easily soluble mercuric salt, $Hg(HCO_2)_2$, gives up carbonic acid upon being gently warmed, and goes into the sparingly soluble mercurous salt, $Hg_2(HCO_2)_2$, which separates in white plates; on increasing the temperature further, this decomposes in its turn into carbon dioxide and metallic mercury. Similarly an aqueous solution of mercuric chloride is reduced by formic acid to the mercurous salt, Hg_2Cl_2.

Formic acid is thus a strong reducing agent:

$$HCO.OH = CO_2 + H_2.$$

It decomposes into carbonic acid and hydrogen when heated alone to 160°, or when brought into contact with finely divided rhodium.

This power of reduction, which distinguishes formic acid from all its higher homologues, may be explained by its close relationship to carbonic acid, and also by the aldehydic character which one can read in its constitutional formula, H—O—CHO.

Acetic Acid,* *acidum aceticum*, $C_2H_4O_2$, was known in the dilute form, as crude wine vinegar, to the ancients. *Stahl* prepared the concentrated acid about 1700. *Glauber* mentions wood vinegar (1648). Its constitution was established by *Berzelius* in 1814.

Occurrence. Salts of acetic acid are found in various plant juices, especially those of trees, and in the perspiration, milk, muscles and excrementa of animals. Ethers of acetic acid also occur, *e.g.* triacetin in croton oil, (see p. 176, and also under glycerine).

Formation. (See p. 162 *et seq.*) Is the final product of the oxidation of a great many compounds, and also of their treatment with alkalies.

The following synthesis is of historical interest. Perchloro-ethylene, C_2Cl_4, which is prepared from CCl_4, *i.e.* from Cl and CS_2, yields with chlorine in presence of water in direct sunlight tri-chloracetic acid, carbon trichloride, C_2Cl_6, being obviously formed as intermediate product, (*Kolbe*, 1843):

$$CCl_3—CCl_3 + 2H_2O = CCl_3—CO_2H + 3HCl.$$

The latter acid is reduced to acetic by nascent hydrogen, (*Melsens*).

Preparation. 1. *From Alcohol.* A dilute aqueous solution of alcohol, containing up to 15 p.c., is slowly converted into acetic acid on exposure to the air and in presence of nitrogenous substances, by the agency of the "mother of vinegar," a film composed of micro-organisms (mainly the *Bacterium aceti*). The acetic fermentation is manifested in the souring of beer or wine, with the production of beer or wine vinegar.

Vinegar is an aqueous solution of acetic acid, usually containing only 3 to 5 p.c., but containing also small quantities of alcohol, of the higher acids, *e.g.* tartaric and succinic, the ethyl ethers of the acids, albuminous matters, etc. It is manufactured on the large scale either, as in France, by the older method in a series of half-full oaken casks, or by the newer quick vinegar process, (*Schützenbach*).

2. *From Wood.* The dry distillation of wood, which is con-

* Ethanoic acid.

ducted in cast-iron retorts, yields (1) gases, *e.g.* hydrogen 15 p.c., methane 11 p.c., carbon dioxide 26 p.c., carbonic oxide 41 p.c., and higher hydrocarbons 7 p.c.; (2) an aqueous solution known as pyroligneous acid which, in addition to acetic acid, contains methyl alcohol, acetone, homologues of acetic acid, and strongly smelling combustible products, (empyreuma); and (3) wood tar, which contains compounds of the nature of carbolic acid. The pyroligneous acid is worked up for acetic acid by converting it into the sodium or calcium salt, heating these—the former up to its melting point and the latter to 200°—to get rid of empyreumatic substances, and then distilling with sulphuric acid.

Properties. Acetic acid is a strongly acid liquid of pungent odour, which feels slippery to the touch and burns the skin, and which solidifies in the cold to large crystalline plates melting at 17°; (Glacial acetic acid). B. Pt. 118°, Sp. Gr. at 15°, 1·055. Its vapour burns with a blue flame. When mixed with water, contraction and consequent increase in density ensue, the maximum point corresponding with the hydrate $CH_3CO_2H + H_2O$, = $CH_3C(OH)_3$, (ortho-acetic acid), which contains 77 p.c. acid and has a Sp. Gr. of 1·075 at 15·5°; after this the specific gravity decreases with further addition of water, so that a 50 p.c. acid has almost the same density as one of 100 p.c. The amount of acid present in a solution is determined either by its Sp. Gr., this contraction being borne in mind, or by titration. The vapour density near the boiling point is much higher than that required by theory, but is normal above 250°. The acid is hygroscopic, and stable towards chromic acid and cold permanganate of potash. It dissolves phosphorus, sulphur and many organic compounds, is corrosive, and gives rise to painful wounds on tender parts of the skin.

Salts. All the neutral salts of acetic acid are soluble in water.

Potassium acetate, $KC_2H_3O_2$; hygroscopic colourless plates. Acid potassium acetate, $C_2H_3O_2K + C_2H_4O_2$, crystallizes from the concentrated acid in glancing mother-of-pearl plates. A salt of the composition $C_2H_3O_2K + 2C_2H_4O_2$ is also known.

Sodium acetate, $NaC_2H_3O_2$, forms transparent easily soluble rhombic prisms, (terra foliata tartari crystallisabilis).

Ammonium acetate, $NH_4C_2H_3O_2$, resembles the potassium salt. It is used in medicine as a sudorific, (Liquor ammonii acetici). Its solution loses ammonia on evaporation, and it yields acetamide when distilled.

Ferrous acetate, $Fe(C_2H_3O_2)_2$, is largely used in the form of "iron liquor" as a mordant in dyeing. The normal ferric salt, $Fe_2(C_2H_3O_2)_6$, which is employed for the same purpose, is obtained when a soluble ferric salt is mixed with sodium acetate. Its solution is deep brown-red in colour, and deposits the iron as basic salt when heated with excess of water:

$$Fe_2(C_2H_3O)_6 + 4H_2O = Fe_2\left\{\begin{matrix}(OH)_4\\(C_2H_3O_2)_2\end{matrix}\right. + 4C_2H_4O_2.$$

It is used in medicine as "liquor ferri acetici."

The analogous aluminium acetate is only known in solution, and finds a wide application as "red liquor" mordant in calico printing and dyeing. Its use depends upon its easy decomposability by water, *e.g.* when exposed to the action of steam, and on the affinity of the residual alumina compound for the colouring matter. It is employed in small doses as an astringent in cases of diarrhœa, etc.

Lead salts. (1) Neutral lead acetate or sugar of lead, $Pb(C_2H_3O_2)_2 + 3H_2O$, is manufactured from sheet lead and acetic acid. It forms colourless lustrous four-sided prisms, which are poisonous and of a nauseous sweet taste. It combines with lead oxide to

(2) Basic salts of alkaline reaction, termed sub-acetates.

The simplest basic salt has the composition $Pb\begin{matrix}\diagup OH\\ \diagdown(C_2H_3O_2)\end{matrix}$,

but there also exist others, *e.g.* $\begin{matrix}Pb\!<\!\!\begin{matrix}OH\\ \end{matrix}\\ >O\\ Pb\!<\!\!(C_2H_3O_2)\end{matrix}$ etc.

Two molecules of acetic acid can combine with as many as five molecules of lead oxide. These basic acetates are used as *Goulard's* lotion, and on the large scale for the preparation of lead white, etc.

Cupric acetate, $Cu(C_2H_3O_2)_2 + 2H_2O$, dark green easily soluble crystals, also forms basic salts (Verdigris). It yields double salts with cupric arseniate, *e.g.* Schweinfurth green.

Silver acetate, $AgC_2H_3O_2$, is a well characterized salt of acetic acid; glancing needles.

Detection of acetic acid. (1) Upon heating an acetate with alcohol and sulphuric acid, the pleasant smelling ethyl acetate is formed; (2) By means of the silver salt; (3) By the odour of cacodyl produced upon heating the potassium or sodium salt with As_2O_3.

Propionic acid, $C_3H_6O_2$, = $CH_3—CH_2—CO_2H$. (*Gottlieb*, 1844.) B. Pt. 141°. Resembles acetic acid.

Formation. From acrylic and lactic acids (see p. 164); also from lactate or malate of calcium by suitable schizomycetes fermentation, (*Fitz*).

Preparation. By the saponification of ethyl cyanide (propionitrile), (1847). (See pp. 118 and 163.)

Calcium chloride separates it from its aqueous solution in the form of an oil, whence its name πρῶτος, the first, and πίων, fat; the first oily acid.

Butyric acids, $C_4H_8O_2$.

(1) **Normal Butyric acid**,* *fermentation butyric acid, propylcarbonic acid*, $CH_3—CH_2—CH_2—CO_2H$.

Occurrence. Free in perspiration, in the juice of flesh, in the contents of the great gut, and in the solid excrementa; as hexyl ether in the oil of the fruit of Heracleum giganteum, as octyl ether in Pastinaca sativa, and to the extent of 2 p.c. as glycerine ether in butter, (*Chevreul*, 1822).

Formation. (See also general modes of formation.) Is produced by the decay of moist fibrin and of cheese (being therefore contained in Limburg cheese), by a Schizomycetes fermentation of glycerine, and of carbohydrates (*Pelouze* and *Gélis; Fitz;* see below). Further, by the oxidation of albuminates with chromic acid, of fats with nitric acid, of conine, etc., and also by the dry distillation of wood.

Preparation. In the "butyric fermentation" of sugar or starch by fission ferments (*e.g. Bacillus butylicus*), $CaCO_3$ or ZnO

* Butanoic acid.

being added at the same time, to combine with the acid formed.

If the fermentation is brought about by impure material (decaying cheese, etc.), lactic acid chiefly is first produced by other micro-organisms, this being then converted into butyric acid by the butyric bacillus.

Properties. Thick liquid of unpleasant rancid odour, in presence of ammonia like that of perspiration, miscible with water, and separating from the aqueous solution on the addition of salts. B. Pt. 163°. Difficultly oxidizable. The calcium salt, $Ca(C_4H_7O_2)_2 + H_2O$, forms glancing plates, and is characterized by being more soluble in cold than in hot water; it therefore separates on warming the concentrated cold aqueous solution. On prolonged heating of the solution, however, it is transformed into the Ca salt of iso-butyric acid. The silver salt, $Ag(C_4H_7O_2)$, crystallizes in glancing plates, slightly soluble in water.

(2) **Iso-butyric acid,*** *di-methyl-acetic acid, iso-propyl-formic acid,* $(CH_3)_2{=}CH-CO_2H$. Is present in the free state in the carob (*Redtenbacher*), in the root of Arnica montana, and as ether in Pastinaca sativa and Roman camomile oil.

It is obtained from isopropyl cyanide (*Erlenmeyer*), by the oxidation of isobutyl alcohol, by the aceto-acetic ether synthesis (p. 215), etc. It is very like fermentation butyric acid, but is more sparingly soluble in water (1 in 5), and boils 9° lower, *i.e.* at 154°. Unlike the latter, however, it is easily oxidized to acetone or acetic acid, and carbonic acid.

The existence of isobutyric acid was predicted by *Kolbe* in 1864 upon theoretical grounds. The calcium salt, $Ca(C_4H_7O_2)_2$, differs from its isomer in being more soluble in hot water than in cold.

Valeric acid, $C_5H_{10}O_2$, exists in the four different modifications which are theoretically possible:

(1) **Normal Valeric acid** (*Pentanoic acid*), *propyl-acetic acid,* $CH_3-(CH_2)_3-CO_2H$, from normal butyl cyanide (*Lieben* and *Rossi*, 1871). Is best prepared from propyl-malonic acid. (See B. 21, Ref. 649; also malonic acid synthesis.) B. Pt. 185°. Only soluble in 27 parts of water.

(2) **Iso-valeric acid,†** *ordinary valeric acid, isopropyl-acetic acid, isobutyl-formic acid,* $(CH_3)_2{=}CH-CH_2-CO_2H$, results from isobutyl cyanide. It is found in the free state and in the form

* 2-Methyl-3-Propanoic acid. † 2-Methyl-4-Butanoic acid.

of ethers in the animal kingdom and in many plants, especially (free) in the valerian root (Valeriana officinalis), and in the angelica root (Angelica archangelica), from which it is obtained by boiling with soda; further, in the blubber of the dolphin (*Chevreul*, 1817), in the berries of Viburnum opulus, in the perspiration from the foot, etc. The natural acid is usually mixed with the active valeric acid, and is therefore optically active; the oxidation of fermentation amyl alcohol by chromic acid yields a similar mixture. When pure it is optically inactive. B. Pt. 175°. It has an unpleasant pungent acid odour, like that of old cheese, and a corrosive action. It is used in medicine. Forms a hydrate with water.

(3) **Methyl-ethyl-acetic acid**, *active valeric acid*,* $\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>CH-CO_2H$, occurs in nature, as already mentioned, and results from the oxidation of the active (—) amyl alcohol; it is in this case (+) optically active, while, if prepared synthetically, *e.g.* by the aceto-acetic ether reaction, it is optically inactive. (See Tartaric acid.) B. Pt. 177°.

(4) **Tri-methyl-acetic acid**, *pivalic acid*, $(CH_3)_3{\equiv}C-CO_2H$, can be prepared from tertiary butyl cyanide, (*Butlerow*, 1873). M. Pt. 35°, B. Pt. 164°. Has an odour like that of acetic acid.

Of the **Hexylic acids**, eight are theoretically possible, and of these seven are already known. The most important among them is **normal caproic acid**, $CH_3-(CH_2)_4-CO_2H$ (*Chevreul*, 1822), which is found in nature, *e.g.* in cocoa-nut oil, Limburg cheese, and as glycerine ether in the butter made from goats' milk, and is produced in the butyric fermentation of sugar, and by the oxidation of albuminous compounds and of the higher fatty acids, etc. Like valeric acid, it has a very unpleasant and persistent odour of perspiration and rancid butter. B. Pt. 205°.

The higher acids which are found in nature are all of normal constitution (see p. 162), and contain for the most part an even number of carbon atoms. Goats' butter contains the acids C_6, C_8, and C_{10}, hence the names **Caproic, Caprilic,** and **Capric** acids, and cocoa nut oil—in addition to those three—the acid C_{12}. This last, **Lauric acid,** is contained more especially in oil of laurels (Laurus nobilis); **Myristic acid,** C_{14}, is present in oil of iris and nutmeg butter (from Myristica moschata); **Arachidic acid,** C_{20}, in the oil of the earth nut (Arachis hypogaea); **Behenic acid,** C_{22}, in oil of ben (Moringa oleifera);

* Hydro-tiglic acid (I.C.N." 2-Methyl-1-Butanoic acid)

B. Unsaturated Acids, $C_nH_{2n-2}O_2$.

		M. Pt.	B. Pt.		M. Pt.	B. Pt.
Acrylic acid, $C_3H_4O_2$		7°	140°	Angelic acid, $C_5H_8O_2$	45°	185°
Crotonic acids, $C_4H_6O_2$	1a	72°	182°	Tiglic acid, $C_5H_8O_2$	65°	198°
	1b	liq.	172°	Pyroterebic acid, $C_6H_{10}O_2$	—	—
	2	16°	160°	Oleic acid, $C_{18}H_{34}O_2$	14°	—

These acids are known as the acids of the oleic series. In their physical properties they nearly resemble the saturated acids, apart from differences in melting point which are sometimes considerable; and they also behave as acids in an analogous manner, but differ characteristically in that they are capable of combining either with two atoms of hydrogen, when heated with hydriodic acid, or with two atoms of halogen or one molecule halogen hydride, to form the saturated acids or their substitution products. Thus oleic acid, $C_{18}H_{34}O_2$, when treated with hydriodic acid and phosphorus, yields stearic acid, $C_{18}H_{36}O_2$, and with bromine, dibromo-stearic acid, $C_{18}H_{34}Br_2O_2$. *Another difference lies in their being easily oxidized.*

In this way they characterize themselves as derivatives of the unsaturated hydrocarbons of the ethylene series, from which one may imagine them to result by the replacement of an atom of hydrogen by carboxyl. They may therefore be termed olefine-carboxylic acids.

Upon the addition of halogen hydride, the halogen does not always attach itself to that carbon atom to which the least hydrogen is bound.

Modes of formation. 1. By oxidation of the corresponding alcohols or aldehydes, *e.g.* acrylic acid from allyl alcohol or acrolein.

2. From the unsaturated alcohols or their iodides, by converting them into the cyanides and saponifying these, *e.g.* crotonic acid from allyl iodide.

Both these methods of formation are analogous to those of the fatty acids.

3. From the mono-halogen substitution products of the saturated fatty acids, by warming with alcoholic potash, some-

times upon simply heating with water. This reaction is analogous to the formation of the olefines from halogen-alkyl; it occurs in the case of those substituted acids which contain the halogen in the β-position to the carboxyl (see p. 183 *et seq.*)

3*a*. From the chloro-, etc., substitution products by backward substitution.

4. From the acids of the lactic series by separation of water:

$$\underbrace{CH_2(OH)—CH_2—COOH}_{\text{Ethylene-lactic acid.}} = \underbrace{CH_2{=}CH—CO_2H}_{\text{Acrylic acid.}} + H_2O.$$

This reaction corresponds with the formation of the olefines from monatomic alcohols.

Constitution and Isomers. The constitution of the unsaturated acids, $C_nH_{2n-2}O_2$, is given when they are regarded as olefine-carboxylic acids. As many isomeric acids as unsaturated alcohols of $n-1$ carbon atoms are therefore possible. (See mode of formation 2, and compare crotonic acid.)

The position of the double bond is established by fusing the acids with potash or soda, *i.e.* by oxidizing them. Oxidation occurs at the point of the double bond (cf. p. 57), and leads to the formation of 2 mols. of a monobasic fatty acid, *e.g.*:

$$CH_3—CH{=}CH—CO_2H + 2KOH + O = 2CH_3—CO_2K + H_2O.$$

Other oxidizing agents, such as chromic and nitric acids, also break them up for the most part in a similar manner, but they carry the oxidation further. By cautious oxidation, on the other hand, *e.g.* with $KMnO_4$ in the cold, the elements of hydrogen peroxide are simply added, and there are formed di-oxy-acids (p. 235) containing an equal number of carbon atoms, for instance, dioxy-stearic, $C_{18}H_{34}(OH)_2O_2$, from oleic acid.

An interesting molecular transformation has been observed upon boiling unsaturated acids with alkali (*Fittig*, B. **24**, 82), the double bond shifting thereby in the direction of the carboxyl; *e.g.* hydrosorbic acid, $CH_3—CH_2—CH{=}CH—CH_2—COOH$, passes into $CH_3—CH_2—CH_2—CH{=}CH—COOH$ (*2-hexene-1-acid*). (For similar cases see the higher homologues of acetylene, p. 65, and the hydro-phthalic acids.) Such changes, which are termed "molecular transformations," are explained by the assumption that atoms or atomic groups (in this case the elements of water) are taken on by the original compound, and given up again in a different manner.

Acrylic acid (*Propenic acid*), *ethylene-carboxylic acid*, $C_3H_4O_2$, = $CH_2{=}CH—CO_2H$ (*Redtenbacher*). **Is prepared by the oxidation of acrolein by oxide of silver, or by the distillation of β-iodo-propionic acid with oxide of lead. (Cf. mode of formation 3.) It is very similar to propionic acid. M. Pt. + 7°, B. Pt.**

139°–140°. Miscible with water and capable of polymerization. It is reduced to propionic acid when warmed with zinc and sulphuric acid, and is broken up, on fusion with alkali, into acetic and formic acids.

Crotonic acids, $C_4H_6O_2$. (1*a*) Ordinary or **solid crotonic acid** (*Butenic acid*), $CH_3—CH=CH—CO_2H$, occurs along with iso-crotonic acid in crude pyroligneous acid, and is prepared from allyl iodide by means of the cyanide, which, instead of having the anticipated formula, $CH_2=CH—CH_2—CN$, has the isomeric one, $CH_3—CH=CH—CN$; this is another case of molecular transformation.

It is also easily prepared by heating malonic acid with para-aldehyde and glacial acetic acid. It crystallizes in woolly needles or large prisms, M. Pt. 72°, B. Pt. 189°, has an odour like that of butyric acid, and is fairly soluble in water.

(1*b*) **Isocrotonic acid**, $CH_3—CH=CH—CO_2H$, which results from the action of sodium amalgam upon chloro-isocrotonic acid, is liquid, and changes into ordinary crotonic acid at 180°. It is present in croton oil. B. Pt. 172°.

Isocrotonic acid was formerly held to have the composition $CH_2=CH—CH_2—CO_2H$. But it shows almost the same chemical behaviour as crotonic acid, *e.g.* on fusion with potash, and is stereo-chemically isomeric with the latter (cf. p. 24). The constitution of both, according to *Wislicenus* (A. **248**, 281), is:—

H—C—CH₃		CH₃—C—H
‖	and	‖
H—C—CO₂H		H—C—CO₂H
Crotonic acid.		Isocrotonic acid.

(2) **Meth-acrylic acid** (*2-Methyl-propenic acid*), $CH_2=C<{CH_3 \atop CO_2H}$, is found in small quantity in Roman camomile oil, and smells like decaying mushrooms. M. Pt. 15°.

When fused with potash, (1) solid crotonic acid yields two molecules of acetic acid, (2) isocrotonic acid yields the same, by a molecular rearrangement, and (3) meth-acrylic acid yields propionic and formic acids.

Angelic acid, $C_4H_7.CO_2H$, is present in the angelica root, and, together with its stereo-isomer, tiglic acid, in Roman camomile oil (cf. A. **250**; **259**, 24; **272**, 1; **273**, 127). M. Pt. 45°.

Pyro-terebic acid, $C_6H_{10}O_2$, $= (CH_3)_2=C=CH—CH_2—CO_2H$, results from the distillation of terebic acid, $C_7H_{10}O_4$.

For investigations of these unsaturated acids and their isomeric relations, still in part unexplained, see *Fittig*, A. **188**, 42; **195**, 56, 128; **255**, 1, 275, etc.; *Wislicenus*, *loc. cit.*

Undecylenic acid, $C_{11}H_{20}O_2$, from castor oil. (See Undecylic acid.)

Oleic acid, $C_{18}H_{34}O_2$ (*Chevreul*), is present as olein in the fatty oils especially, *e.g.* olive, almond and train oils. Colourless oil, solidifying to white needles in the cold. M. Pt. 14°. Cannot be volatilized without decomposition. It is tasteless and odourless, and has no action upon litmus, but quickly becomes yellow and acid by oxidation in the air, and also

acquires a rancid odour. Its lead salt is soluble in ether. It yields on fusion with potash the saturated acids $C_{16}H_{32}O_2$ and $C_2H_4O_2$, and on oxidation with nitric acid the acids from $C_2H_4O_2$ to $C_{10}H_{20}O_2$, besides dibasic acids. Nitrous anhydride converts it into the isomeric crystalline **Elaïdic acid.** M. Pt. 45°.

Its constitution is probably expressed by the formula:

$$CH_3—(CH_2)_{13}—CH=CH—CH_2—CO_2H.$$

Erucic acid, $C_{22}H_{42}O_2$, in rape seed oil (Brassica campestris).

Related to the above are:

Linoleic acid, $C_{18}H_{32}O_2$, which belongs to the next series, and which is present as glycerine ether in the drying oils, *e.g.* linseed, hemp and nut oils; also **Ricinoleic acid,** $C_{18}H_{34}O_3$, whose glycerine ether forms castor oil. M. Pt. 17°. This acid is an excellent material for the preparation of oenanthol, undecylenic acid, caprylic alcohol, and sebacic acid. The so-called ricinoleic-sulphuric acid, which is prepared by treating castor oil with sulphuric acid, is extensively used in the Turkey-red manufacture.

C. Propiolic Acid Series, $C_nH_{2n-4}O_2$.

The acids of this series again contain two atoms of hydrogen less than those of the former, and are to be regarded as carboxylic acids of the acetylene hydrocarbons, *e.g.* propiolic acid, $CH{\equiv}C—CO_2H$, as acetylene-carboxylic acid. They can accordingly be prepared by the addition of CO_2 to the sodium derivatives of the acetylenes (analogously to mode of formation 4 of the saturated acids, p. 163).

They closely resemble the unsaturated acids which have been already described, but differ from them by their capability of combining first with two, and finally with four monovalent atoms of hydrogen or halogen, and of yielding explosive compounds with ammoniacal silver and copper solutions. There are, however, acids of the formula $C_nH_{2n-4}O_2$ which do not possess this last peculiarity, viz., those which are derived, not from the homologues of acetylene proper, but from their isomers, and which therefore contain two double bonds instead of a triple one.

The most important member of the series is Propiolic or Propargylic acid,* $C_3H_2O_2$, $= CH{\equiv}C—CO_2H$, which corresponds to propargyl alcohol, and is prepared by warming an

* Propiolic acid.

aqueous solution of the acid potassium salt of acetylene-dicarboxylic acid, the latter being itself obtained from dibromo-succinic acid. (See p. 256, also B. 18, 677.) In its physical properties it is very like propionic acid, forms silky crystals below 6°, and boils at 144°. It is readily soluble in water and alcohol, and becomes brown in the air. It gives, even in dilute solution, the characteristic explosive silver precipitate.

Tetrolic acid, $C_4H_4O_2$. M. Pt. 76° (from β-chloro-crotonic acid and aqueous potash), and :—

Sorbic acid, $C_6H_8O_2$, the latter of which is contained in the juice of the unripe sorb apple (Sorbus aucuparia), have both relatively high melting and boiling points. The higher acids of the series are for the most part distinguished by the termination "olic," *e.g.* **Undecolic acid**, $C_{11}H_{20}O_2$, **Palmitolic acid**, $C_{16}H_{28}O_2$, **Stearolic acid**, $C_{18}H_{32}O_2$, **Behenolic acid**, $C_{22}H_{40}O_2$; *they result from the corresponding unsaturated acids*, $C_nH_{2n-2}O_2$, *by the* addition of Br_2 and separation of 2HBr.

Appendix. A. **Di-acetylene-mono-carboxylic acid** (*Penta-diinic acid*), $CH{\equiv}C—C{\equiv}C—CO_2H$ appears to exist. (B. **18**, 681.)

D. Halogen Substitution Products of the Monobasic Acids.

The saturated monobasic acids yield substitution products when acted upon by chlorine or bromine, or—better—bromine and phosphorus, *e.g.*:

	M. Pt.	B. Pt.		M. Pt.	B. Pt.
$CH_3—CO_2H$ Acetic acid, . .	17°	118°	$CH_3—CH_2—CO_2H$ Propionic acid, .	liq.	140°
$CH_2Cl—CO_2H$ Mono-chlor-acetic acid, ...	62°	186°	$CH_3—CHCl—CO_2H$ α-chloro-propionic acid, ...	liq.	186°
$CHCl_2—COOH$ Di-chlor-acetic acid, ...	liq.	191°	$CH_2Cl—CH_2—CO_2H$ β-chloro-propionic acid, ...	40°	
$CCl_3—COOH$ Tri-chlor-acetic acid, ...	52°	195°	$C_2H_3Br_2—CO_2H$ Di-bromo-propionic acids, etc.		

The acids poorer in hydrogen also yield similar substitution products:

	M. Pt.	
$CH_2=CH-CO_2H$ Acrylic acid, ...	7°	$CH\equiv C-CO_2H$ Propiolic acid.
$CH_2=CCl-CO_2H$ α-Chlor-acrylic acid, . . .	65°	$CI\equiv C-CO_2H$ Iodo-propiolic acid, etc.
$CHCl=CH-CO_2H$ β-Chlor-acrylic acid, . . .	84°	

These compounds are likewise monobasic acids, being often very similar to the mother substance, and exceeding it in acidity. Since their acid nature remains unaltered, they still contain the carboxyl group; the halogen has therefore replaced the hydrogen of the hydrocarbon radicle. They may also be looked upon as haloid substitution products of the hydrocarbons, in which one atom of hydrogen is replaced by carboxyl:

$CH_3 . Cl$, Chloro-methyl. $CH_2{}^{Cl}_{CO_2H}$, Chlor-acetic acid.

The modes of formation and properties of these substituted acids also coincide with this view. Thus, while they show a perfectly analogous behaviour to that of the non-substituted acids, forming salts, ethers, chlorides, anhydrides and amides, their halogen atoms are as easily exchangeable, *e.g.* for OH, CN, or SO_3H, as those of the substitution products of the hydrocarbons. (See p. 68.)

Isomers and Constitution. While in each case only one mono-, di-, etc., haloid acetic acid exists, two isomeric mono-haloid propionic acids are known (see table). This is readily explicable from the fact that in propionic acid,

$$\underset{\beta}{CH_3}-\underset{\alpha}{CH_2}-CO_2H,$$

the two α-hydrogen atoms are differently bound from the three β-ones, the former being attached to the carbon atom nearest to the carboxyl and the latter to that one farthest from it. According to theory, therefore, with which the observed facts agree, the following two isomers are possible:

$$\underbrace{CH_3{-}CHX{-}CO_2H}_{\alpha\text{-Haloid-propionic acid.}} \text{ and } \underbrace{CH_2X{-}CH_2{-}CO_2H.}_{\beta\text{-Haloid propionic acid.}}$$

These acids yield two isomeric lactic acids by exchange of their halogen for hydroxyl, thus:

$$\underbrace{CH_3{-}CH(OH){-}CO_2H}_{\text{Common lactic acid.}} \text{ and } \underbrace{CH_2(OH){-}CH_2{-}CO_2H.}_{\text{Ethylene lactic acid.}}$$

The constitution of both of these lactic acids follows from their other modes of formation, (see p. 229, et seq.). The position of the halogen in the α- and β- substituted propionic acids is thus also fixed.

Those substituted acids which contain the halogen bound to the α-carbon atom, *i.e.* to the carbon atom next to the carboxyl, are termed α-acids, and the others β, γ, etc., acids, the successive carbon atoms in their order from the carboxyl group being designated as α, β, γ, etc.

We thus distinguish, for instance, between α-, β- and γ- chloro-butyric acids, αα-, αβ- and ββ- dibromo-propionic acids etc.

Two geometrically isomeric forms of the mono-chloro- and -bromo-crotonic acids are known (A. **248**, 281), being derived from crotonic and iso-crotonic acids.

A chlorinated Formic acid, $Cl{-}CO_2H$, is incapable of existence; its derivatives are described as derivatives of chloro-carbonic acid.

Formation. (*a*) Of the saturated substituted acids.

1. Chlorine and bromine can substitute directly, the halogen taking up the α-position to the carboxyl.

In trimethyl-acetic acid $(CH_3)_3{\equiv}C{-}CO_2H$, which contains no hydrogen in the α-position, bromine therefore does not substitute (B. **23**, 1594).

2. From oxy-acids of the glycollic series by the action of PCl_5, HBr, etc.

3. By the addition of halogen or halogen hydride to the unsaturated acids.

(*b*) Of the unsaturated substituted acids: *e.g.* From di- or poly-brominated etc. acids, by the separation of HCl, HBr or HI.

Behaviour. 1. For the replacement of chlorine, bromine and iodine by hydroxyl, see p. 222. This exchange takes place with more difficulty in the α-mono-chloro-substituted acids than in the corresponding bromine and iodine com-

pounds, but more easily than in the case of the chloro-alkyl compounds, and it is effected by means of moist oxide of silver, or frequently by prolonged boiling with water alone, (A. 200, 75). In this way monochlor-acetic yields glycollic acid:

$$\begin{matrix} CH_2Cl \\ | \\ CO_2H \end{matrix} + H_2O = \begin{matrix} CH_2.OH \\ | \\ CO_2H \end{matrix} + HCl.$$

β-Halogen acids on the other hand lose halogen hydride upon being boiled with water, and give rise to unsaturated acids, together with CO_2 and olefines C_{n-1}. γ-Halogen acids break up under these conditions (even with cold soda solution) into HCl, etc., and a lactone, *i.e.* an anhydride of a γ-oxy-acid, (see these; c.f. *Fittig*, A. **208**, 116).

2. Upon heating with cyanide of potassium, cyano-fatty acids are produced:

$$CH_2Cl—CO_2K + KCN = \underbrace{CH_2{<}^{CN}_{CO_2K}}_{\text{Potassium cyano-acetate.}} + KCl.$$

These compounds are on the one hand monobasic acids, and on the other cyanides, *i.e.* nitriles of the acids, and they consequently yield dibasic acids upon saponification, in the above case malonic acid, $CH_2{<}^{CO_2H}_{CO_2H}$.

3. They form sulphonic acids with sodium sulphite, *e.g.*:

$$CH_2Cl—CO_2Na + Na.SO_3Na = \underbrace{CH_2{<}^{SO_3Na}_{CO_2Na}}_{\text{Sodium sulpho-acetate.}} + NaCl.$$

These latter are compounds which, apart from the acid character they derive from the carboxyl, are actual sulphonic acids, like ethyl-sulphonic acid, and are thus dibasic. Their sulpho-group can however be replaced by OH on boiling with alkalies.

4. With $AgNO_2$, under favourable conditions, nitro-derivatives of the fatty acids are formed, which yield amido-acids on reduction, (p. 227).

4a. Iso-nitroso derivatives of the fatty acids, e.g. α-iso-nitroso-propionic acid, $CH_3—C(N.OH)—CO_2H$, are also known; they are formed by the

action of hydroxylamine on the ketonic acids, for instance, pyroracemic acid, $CH_3—CO—CO_2H$, and also yield amido-acids upon reduction.

The compounds mentioned under 2 and 4 are to be regarded as derivatives of the alcoholic acids, just as the nitro-alkyls, alkyl cyanides and alkyl-sulphonic acids are derivatives of the alcohols.

The chlorinated acetic acids are formed by the direct substitution of acetic acid, or, better, of acetyl chloride, chlorinated acetyl chlorides ensuing in the latter case as intermediate products.

Mono-chlor-acetic acid (*Chloro-ethanoic acid*), $CH_2Cl.CO_2H$, is got by chlorinating acetic acid, preferably in the presence of acetic anhydride, sulphur or phosphorus. It forms rhombic prisms or tables and corrodes the epidermis. **Di-chlor-acetic acid**, $CHCl_2.CO_2H$, is more conveniently obtained by warming chloral hydrate with potassium cyanide (B. **10**, 2120), and **Tri-chlor-acetic acid**, $CCl_3.CO_2H$, by oxidizing chloral hydrate with nitric acid. The former decomposes with boiling alkali to oxalic and acetic acids, and the latter to chloroform and carbon dioxide. Backward substitution re-converts tri-, di-, and mono-chlor-acetic acids into acetic acid (*Melsens*, 1842).

Sulpho-acetic acid, $CH_2(SO_3H)—CO_2H$. Deliquescent prisms containing 1½ mols. H_2O of crystallization; yields salts which crystallize well. **Cyan-acetic acid**, $CH_2(CN)—CO_2H$, is a crystalline substance melting at 65°–66° and easily soluble in water; it decomposes into aceto-nitrile, $CH_3—CN$, and CO_2 upon heating, and yields malonic acid on saponification.

α-Chloro-propionic acid, $CH_3—CHCl—CO_2H$, is obtained by the action of PCl_5 upon lactic acid, and decomposition of the lactyl chloride, $CH_3—CHCl—COCl$, at first formed, by water. **β-Iodo-propionic acid**, $CH_2I—CH_2—CO_2H$, is prepared by acting upon glyceric acid, $CH_2(OH)—CH(OH)—CO_2H$, with iodide of phosphorus (exchange of 2OH for 2I and of I for H); also by acting on acrylic acid with hydriodic acid. It forms colourless six-sided tables of a peculiar odour; M. Pt. 82°. The two **Cyano-propionic acids**, $C_2H_4(CN)—CO_2H$, give the two succinic acids when saponified.

Chloro- and **Bromo-crotonic acids.** For formation and isomerism see p. 184 *et seq.* **β-Chloro-crotonic acid** (*2-Chloro-2-Butenic acid*) (M. Pt. 94°) results from the addition of HCl to tetrolic acid, and, according to *Wislicenus*, must have the following configuration, since, through the addition to the triple carbon linking, only one structure with a double linking can result, *which contains the added atoms in plano-symmetric position:*

$$\begin{array}{c}Cl—C—CH_3\\ \| \\ H—C—CO_2H;\end{array}$$

here the β-position of the chlorine is easily demonstrable. Since solid crotonic acid results by the replacement of the chlorine by hydrogen, the stereo-constitution, given on p. 180, follows.

The stereo-isomeric **β-Isochloro-crotonic acid** is formed by the action of PCl_5 on aceto-acetic ether, and treatment of the product with water.

VII. ACID DERIVATIVES.

Summary.

$C_2H_5.OH$	Alcohol	$C_2H_3O.OH$	Acetic acid
$C_2H_5.ONa$	Sodium ethylate	$C_2H_3O.ONa$	Sodium acetate
$C_2H_5.O.(C_2H_5)$ or $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O$	Ethyl ether	$C_2H_3O.O.(C_2H_5)$	Ethyl acetate
		$\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}>O$	Acetic anhydride
$C_2H_5.Cl$	Ethyl chloride	$C_2H_3O.Cl$	Acetyl chloride
$C_2H_5.SH$	Mercaptan	$C_2H_3O.SH$	Thiacetic acid
$C_2H_5.NH_2$	Ethylamine	$C_2H_3O.NH_2$	Acetamide

These derivatives result by methods of which some are perfectly analogous to the modes of formation of the corresponding alcoholic derivatives, but they differ characteristically from these by being less stable towards saponifying agents.

A number of other derivatives, viz., amido- and imido-chlorides, thiamides, imido-thio-compounds and amidines are peculiar to the acids:

$CH_3—CCl_2—NHR$*	Amido-chlorides	$CH_3—C(NH)OH$	Imido-compounds
$CH_3—CCl=NR$	Imido-chlorides	$CH_3—C(NH)SR$	Imido-thio- ,,
$CH_3—CS—NH_2$	Thiamides	$CH_3—C(NH)(NH_2)$	Amidines

* R signifies an alcohol radicle or an analogous group such as C_6H_5—, phenyl. (See aromatic compounds.)

These compounds are also characterized by being easily saponifiable.

A. Ethers (Esters) of the Fatty Acids.

By the replacement of the typical hydrogen of a fatty acid by an alcohol radicle, ethers are produced which are perfectly analogous to the ethers of the mineral acids in their properties, and which are also obtained by analogous methods. Since these correspond to the salts of the acids, they are often designated in a similar way, *e.g.* acetic ethyl ether = "ethylic acetate."

Modes of formation. (1) By direct action of the acid upon the alcohol:

$$C_2H_5.OH + C_2H_3O.OH = \underbrace{C_2H_5.O.C_2H_3O}_{\text{Ethylic acetate.}} + H_2O.$$

Only a few acids thus react with alcohol by itself to form ethers in quantity, for reasons similar to those already given for mineral acids at p. 108.

In the preparation of ethers it is therefore necessary to provide against a re-saponification of the ether after it is formed, which is done as above described (loc. cit.). The method of etherification by leading hydrochloric acid gas into a mixture of acid and alcohol is especially applicable. The ethers are also obtained directly from the acid nitriles by passing hydrochloric acid into their warm alcoholic solution. The limit of etherification agrees with the *Guldberg-Waage* law of the action of mass, (*Berthelot, Menschutkin.*)

(2) By the action of the acid chlorides upon the alcohols or their sodium compounds (cf. p. 109):

$$C_2H_3O.Cl + C_2H_5.OH = C_2H_3O.O.C_2H_5 + HCl.$$

(3) By the action of the halogen alkyls upon the salts of the acids (cf. p. 109):

$$C_2H_5Cl + C_2H_3O.ONa = C_2H_5.O.(C_2H_3O) + NaCl.$$

Ethers are likewise obtained by heating the salts of fatty acids with alkyl sulphates.

Properties. The ethers of the monobasic fatty acids are for the most part neutral liquids which volatilize without decomposition, only those of them which contain a small number of carbon atoms in the molecule being soluble in water, *e.g.* acetic

ether (1 : 14). They undergo saponification upon heating or, more generally, superheating with water, or upon boiling with alkalies or acids.

It often suffices for saponification simply to mix the ether with alcoholic potash or soda, or to allow it to stand for a lengthened period with water.

The compound ethers are very active chemically, since they readily exchange the group $—OC_2H_5$, *i.e.* —OR, for another group, yielding with ammonia, for instance, amides (p. 195). Phosphorus pentachloride decomposes them into the chloride of the alcohol and that of the acid, the oxygen of the hydroxyl being exchanged for two atoms of chlorine.

Sodium methylate combines with the ethers to form unstable compounds, $R—C\begin{matrix}\diagup ONa \\ —OCH_3 \\ \diagdown OR'\end{matrix}$, which are derivatives of "ortho acids." (See p. 163; also B. 20, 646.) Certain compound ethers interact with one another, so as to exchange their alcohol radicles (B. 23, Ref. 468).

The odour and taste of many of the ethers is so agreeable that they are manufactured upon a large scale, and employed as fruit ethers or fruit essences.

Ethyl formate, *formic ethyl ether,* $H.CO.OC_2H_5$. B. Pt. 55°. Is employed in the manufacture of artificial rum or arrak.

Ethyl acetate, *acetic ether,* $C_2H_3O.OC_2H_5$. B. Pt. 75°. Is used internally as a medicine.

Amyl acetate, $C_2H_3O.OC_5H_{11}$. B. Pt. 148°. The alcoholic solution of this forms the ether of pears.

Ethyl butyrate, $C_4H_7O.OC_2H_5$, is the ether of pine apples.

Iso-amyl iso-valerate, $C_5H_9O.OC_5H_{11}$, B. Pt. 196°, finds application as apple oil or apple ether.

Cetyl palmitate, $C_{16}H_{31}O_2(C_{16}H_{33})$, **Ceryl cerotate,** $C_{27}H_{53}O_2(C_{27}H_{55})$, and **Mellissic palmitate,** $C_{16}H_{31}O_2(C_{30}H_{61})$. (See Wax Varieties, p. 176.)

When the ethers of the acids of high molecular weight are distilled under the ordinary pressure and not in a vacuum, they break up into olefine and fatty acid. (See p. 58.)

Among the ethers of the haloid-substitution acids may be mentioned ethyl monochlor-acetate, $CH_2Cl—CO_2(C_2H_5)$, B. Pt. 145°, and ethyl trichlor-acetate, $CCl_3—CO_2(C_2H_5)$, B. Pt. 164°.

Isomers. All those ethers of the different monatomic

saturated alcohols and acids are isomeric, the sums of whose carbon atoms are equal to one another; thus methyl butyrate is isomeric not only with ethyl propionate but also with propyl acetate and with butyl formate. Further, all ethers are isomeric with the monobasic acids which contain an equal number of carbon atoms with them, *e.g.* the ethers just mentioned are isomeric with valeric acid. (See Metamerism, p. 102.)

Further cases of isomerism occur when the alcohol on the one hand, or the acid on the other, is unsaturated, *e.g.* allyl propionate and propyl acrylate.

B. Chlorides of the Acid Radicles.

(Acid Chlorides, or Chloro-anhydrides of the Acids.)

Among the halogen compounds of the acid radicles those of chlorine are the most important.

Formation. (1) From the acid and hydrochloric acid by means of phosphoric anhydride; this method is of theoretical value only:

$$C_2H_3O.OH + HCl = C_2H_3O.Cl + H_2O.$$

(2) By the action of chlorine upon the aldehydes:

$$CH_3.CHO + Cl_2 = CH_3.COCl + HCl.$$

(3) By the action of the chlorides of phosphorus, PCl_3 and PCl_5, upon the acids or their salts:

$$C_4H_7O.OH + PCl_5 = C_4H_7O.Cl + POCl_3 + HCl.$$

The acid chloride is separated from the $POCl_3$ formed at the same time by fractional distillation. In the case of acetic acid PCl_3 is conveniently used, being warmed with the free acid upon the water-bath:

$$3C_2H_3O.OH + PCl_3 = 3C_2H_3O.Cl + PO_3H_3.$$

Phosphorus oxychloride, $POCl_3$, may also be allowed to act upon the alkaline salts of the acids; when the latter are present in excess, acid anhydrides are produced (p. 192).

(4) Several of the acid bromides result from the bromo-derivatives of the olefines by the absorption of oxygen from the air, thus $CBr_2{=}CH_2$ yields $CH_2Br{-}COBr$, bromo-acetyl bromide.

(5) From Phosgene, $COCl_2$, and zinc alkyl (see p. 164).

Properties. The acid chlorides are suffocating liquids which fume in the air, distil without decomposition, and are reconverted by water into the corresponding acids and hydrochloric acid, for the most part at the ordinary temperature:

$$C_2H_3O.Cl + H_2O = C_2H_3O.OH + HCl.$$

They react with alcohol and the alcoholates to form ethers, with the salts of the acids to form anhydrides, and with ammonia to form amides. Sodium amalgam reduces them to aldehydes and alcohols. With zinc alkyl they yield ketones or tertiary alcohols, according to the conditions of the experiment. (Cf. pp. 152 and 86.)

On treatment with silver cyanide, the cyanides of the acid radicles are formed, *e.g.* **Acetyl cyanide**, $CH_3.CO.CN$, from acetyl chloride. These are of great importance for the synthesis of the ketonic acids, being saponified by concentrated hydrochloric acid in the same way as the cyanides of the alcohol radicles, with transformation of $-CN$ into $-CO.OH$; dilute hydrochloric acid, on the contrary, decomposes them into the original acid and HCN. When it is attempted to isolate the acid radicle by removing the halogen, it is found that two radicles unite together with formation of *double ketones*, $R{-}CO{-}CO{-}R$ (see p. 238).

Acetyl chloride (*Ethanoyl chloride*), $CH_3.COCl$. Mobile colourless liquid of suffocating odour. B. Pt. 55°; Sp. Gr. at 0°, 1·13. Decomposes violently with water, with ebullition, and with strong ammonia with explosive rapidity. Is a reagent of exceptional importance, since it serves for the conversion of the alcohols and ammonia compounds (primary and secondary amines) into their acetic derivatives, and thus frequently leads to the explanation of the chemical nature of the substance under investigation (see p. 124).

Among the homologues of acetyl chloride which are known are **Propionyl chloride**, $C_2H_5.COCl$, **Butyryl chloride**, $C_3H_7.COCl$, **Isovaleryl chloride**, $C_4H_9.COCl$, and **Palmityl chloride**, $C_{15}H_{31}.COCl$;

likewise **Acetyl bromide**, $CH_3.COBr$, B. Pt. 81°, and **Acetyl iodide**, $CH_3.COI$, (from iodine, phosphorus and acetic anhydride). The chloride of formic acid, $HCOCl$, is however unknown, since it immediately breaks up into CO and HCl when its preparation is attempted. As examples of chlorides of substituted acids we may take **Mono-chlor-acetyl chloride**, $CH_2Cl.COCl$, B. Pt. 106°, and **Lactyl chloride**, $CH_3-CHCl-COCl$.

C. Acid Anhydrides.

Corresponding to the monobasic fatty acids there are anhydrides, which are derived from two molecules of the acid with the separation of a molecule of water, *e.g.*:

$$\begin{matrix} CH_3.CO.OH \\ CH_3.CO.OH \end{matrix} = \begin{matrix} CH_3-CO \\ CH_3-CO \end{matrix}\!\!>O + H_2O.$$

They may also be considered as oxides of the acid radicles, for instance, $(C_2H_3O)_2O$, = Acetyl oxide.

Preparation. 1. They do not as a rule result from the acids by direct abstraction of water, but, *e.g.*, by the action of acid chlorides upon the alkaline salts of the acids:

$$C_2H_3OCl + C_2H_3O.ONa = \begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\!\!>O + NaCl.$$

1ª. By the direct action of phosphorus oxychloride upon the alkaline salts of the acids, acid chlorides being formed in the first instance, (see p. 190).

2. By the action of phosgene on the acids, (B. **17**, 1286):

$$2CH_3.CO.OH + COCl_2 = (CH_3-CO)_2O + CO_2 + 2HCl.$$

2ª. The *anhydrides of the higher acids are conveniently* prepared by treating these with acetyl chloride, (B. **10**, 1881):

$$2R.CO.OH + CH_3.COCl = (R.CO)_2O + CH_3.COOH + HCl.$$

Properties. The majority of the acid anhydrides are liquids, but those of higher molecular weight solids, of neutral reaction and soluble in alcohol and ether. They are insoluble in water, but are gradually decomposed by it into acid hydrates. On warming with alcohol, compound ethers are formed, and by

the action of ammonia, amides. They yield with HCl gas, acid chloride and free acid:

$$(C_2H_3O)_2O + HCl = C_2H_3O.Cl + C_2H_3O.OH.$$

Acetic anhydride,* $(C_2H_3O)_2O$, is a mobile liquid of suffocating odour, boiling at 137°, and having a Sp. Gr. at 20° of 1·073. Like acetyl chloride it is a reagent of great importance, since it converts primary and secondary ammonia derivatives into acetyl compounds.

Intermediate or **Mixed anhydrides** containing two different acid radicles are also known, (*Gerhardt, Williamson*), *e.g.* $\left.\begin{matrix}C_2H_3O\\C_5H_{11}O\end{matrix}\right\}O$. They break up into two simple anhydrides upon distillation.

We are likewise acquainted with peroxides of the acid radicles, *e.g.* **Acetyl peroxide**, $(C_2H_3O)_2O_2$, a thick liquid insoluble in water, which acts as a strong oxidizing agent and explodes upon warming; it is prepared by the action of barium peroxide, BaO_2, upon acetic anhydride.

D. Thio-acids and Thio-anhydrides.

Just as in the alcohols and ethers, so in the acids and their anhydrides is oxygen replaceable by sulphur. There are thus theoretically possible: (1) Thio-acids ("O.N." *Thiolic acids*), *e.g.* thiacetic acid, $CH_3.CO.SH$, and their isomers ("O.N." *Thionic acids*), *e.g.* $CH_3.CS.OH$ (as yet unknown); (2) Thio-anhydrides, *e.g.* acetyl sulphide $(C_2H_3O)_2S$; (3) Di-thio-acids, *e.g.* $CH_3CS.SH$ (*Ethane-thionic-thiolic acid*), (as yet only known in the aromatic series).

Thiacetic acid (*Ethane-thiolic acid*), $C_2H_3O.SH$, is a colourless liquid boiling below 100°, which smells of acetic acid and sulphuretted hydrogen, and readily decomposes with water into those two components. It is prepared from acetic acid and phosphorus pentasulphide, P_2S_5. The other thio-compounds are likewise easily saponifiable, with formation of acetic and hydrosulphuric acids.

* Ethanoic anhydride.

Ethers of thiacetic acid are also known, *e.g.* **ethyl thiacetate**, $CH_3CO.S.C_2H_5$, which is obtained from acetyl chloride and sodium mercaptide; they are liquids which distil without decomposition, and are easily saponified back to acid and mercaptan.

E. Amides.

By the replacement of the hydrogen in ammonia by acid radicles or, in other words, by the replacement of the acid hydroxyl by amidogen, etc., amides result, these being primary, secondary, or tertiary, according to the number of hydrogen-atoms substituted:

$$\underbrace{NH_2.C_2H_3O}_{\text{Acetamide.}} \qquad \underbrace{NH(C_2H_3O)_2}_{\text{Di-acetamide.}} \qquad \underbrace{N(C_2H_3O)_3}_{\text{Tri-acetamide.}}$$

Of these the primary amides are the most important. They are solid crystalline compounds, at first soluble in water but becoming insoluble with increasing carbon, and soluble in alcohol and ether. They distil without decomposition (*in vacuo*, if necessary). They differ characteristically from the amines in being easily saponifiable, breaking up into their components, acid and ammonia, when superheated with water or when boiled with alkalies or acids.

Alkylated amides are compounds derived from ammonia by the replacement of its hydrogen by alcoholic and acid radicles at the same time, *e.g.* ethyl acetamide, $C_2H_3O.NH.(C_2H_5)$ and di-methyl acetamide, $(CH_3)_2N.C_2H_3O$. They are to be regarded as acid, *e.g.*, acetyl-derivatives of the nitrogen bases of alcohol radicles; thus, ethyl acetamide is the same as acetyl ethylamine, $C_2H_5.NH(C_2H_3O)$.

Modes of formation. 1. By the dry distillation of the ammonium salts of the fatty acids or, better, by heating them in a closed vessel to 230° (*Hofmann*, B. 15, 977), thus:

$$CH_3CO.ONH_4 = CH_3CO.NH_2 + H_2O.$$

2. By addition of water to the cyanides of the alcohol radicles containing one atom of carbon less than themselves:

$$CH_3—CN + H_2O = CH_3—CO.NH_2.$$

This assimilation of water is frequently effected by dissolving the nitrile in concentrated sulphuric acid, or in acetic and concentrated sulphuric acids, or by shaking with concentrated hydrochloric acid in the cold; also, and often quantitatively, by hydrogen peroxide, H_2O_2.

3. By the action of acid chlorides upon aqueous ammonia or solid ammonium carbonate; if amines are employed here, in place of ammonia, alkylated amides result:

$$CH_3.COCl + 2NH_3 = CH_3.CONH_2 + NH_4Cl.$$

3ª. In an analogous manner from acid anhydrides:

$$(C_2H_3O)_2O + 2NH_3 = C_2H_3O.NH_2 + C_2H_3O.ONH_4.$$

4. By heating compound ethers with ammonia, sometimes even on shaking in the cold:

$$CH_3.CO.OC_2H_5 + NH_3 = CH_3.CONH_2 + C_2H_5OH.$$

5. The secondary and tertiary amines result upon heating the acids or anhydrides with their nitriles:

$$CH_3.CN + CH_3.COOH = (CH_3.CO)_2NH;$$
$$CH_3.CN + (CH_3.CO)_2O = (CH_3.CO)_3N.$$

Behaviour. 1. The amides, although derivatives of ammonia, are hardly basic, the strongly positive character of the hydrogen atoms of the ammonia being cancelled by the entrance of the negative acid radicle. Still the primary amides are capable of forming addition-compounds with some acids, *e.g.* acetamide yields the compound $(C_2H_3O.NH_2)_2HCl$, "acetamide hydrochloride"; these are however unstable, and are decomposed for the most part by water alone. On the other hand the hydrogen of the amido-group can be replaced by particular metals, especially mercury (also sodium; cf. B. **23**, 3037), the amides therefore playing the part of weak acids in the compounds so obtained, *e.g.* mercury acetamide $(CH_3.CONH)_2Hg$.

2. The amides are readily saponifiable. When they also contain alcoholic radicles, only the acid and not the alcohol radicle is separated on saponification, in accordance with the fact that the amine bases are not saponifiable, thus:

$$C_2H_3O.NHC_2H_5 + NaOH = C_2H_3O.ONa + C_2H_5NH_2.$$

3. Nitrous acid converts the primary amides into the corresponding acids, with liberation of nitrogen:

$$C_2H_3O.NH_2 + NO_2H = C_2H_3O.OH + N_2 + H_2O.$$

This reaction is a general one, and corresponds exactly with the action of nitrous acid upon the primary amines.

4. Upon heating the primary amides with phosphorus pentoxide, P_2O_5, nitriles are produced (see p. 117). These are also obtained upon heating with P_2S_5, and PCl_5, amidochlorides or thiamides being in this case formed as intermediate products, (see pp. 198 and 199).

5. If bromine in the presence of alkali is allowed to act upon primary amides, there ensue in the first instance amides whose NH_2-hydrogen is replaced by halogen, *e.g.* $CH_3.CO.NHBr$, aceto-bromamide, (colourless rectangular plates), and $CH_3.CO.NBr_2$:

$$CH_3—CO.NH_2 + Br_2 = CH_3—CO.NHBr + HBr, \text{etc.}$$

These yield peculiar urea derivatives with more amide and alkali, *e.g.* methyl-acetyl-urea, $CO\begin{cases} NH.COCH_3 \\ NH.CH_3 \end{cases}$, which are split up by further addition of alkali in the normal manner, with formation of amines—in this case $CH_3.NH_2$—containing one atom of carbon less than the original product. (See urea.) This is an excellent method for preparing the amines from C_1 to C_5, but less desirable for those from C_6 onwards, as in the case of the higher molecular compounds the production of amine diminishes, a nitrile being formed instead by the further action of the bromine, (see below). Such nitriles C_n, in which $n > 5$, can therefore be obtained directly from the amine by the action of bromine and alkali upon it, thus:

$$\begin{aligned} C_7H_{15}—CH_2.NH_2 + 2Br_2 &= C_7H_{15}—CH_2.NBr_2 + 2HBr \\ &= C_7H_{15}.CN + 4HBr. \end{aligned}$$

(Reversal of the *Mendius* reaction, p. 123; cf. *Hofmann*, B. **15**, 407, 752; **17**, 1407, 1920; **18**, 2737).

Since these nitriles go on saponification into acids containing one atom of carbon less than the amide originally taken, this reaction renders it possible to descend in the series successively

from one acid to another (pp. 166 and 160). This has been done in the case of the normal acids from C_{14} to C_1, and it furnishes a further proof of their normal constitution.

Constitution. The properties and modes of formation of the amides agree with the constitutional formula:

$$R{-}C\begin{matrix}\nearrow O \\ \searrow NH_2.\end{matrix}$$

But, besides this, the following one is conceivable, in favour of which certain arguments have recently been adduced (B. **22**, 3273; **23**, 103; **25**, 1435):

$$R{-}C\begin{matrix}\nearrow OH \\ \searrow NH.\end{matrix}$$

This last formula easily passes into the first by the migration of one hydrogen atom, and most of the reactions of the simple amides are explicable almost equally well by either formula.

The case of the alkylated amides is, however, different. The formulae:

$$\text{(I.) } R{-}C\begin{matrix}\nearrow OR' \\ \searrow NH\end{matrix} \quad \text{and} \quad \text{(II.) } R{-}CO.NHR'$$

represent chemical isomers. A transformation of one of these into the other could only take place by the detachment of the alkyl R′ from the oxygen or the nitrogen, an event which experience has shown does not occur. The compounds of the type I. are therefore essentially distinct from those of the type II. They will be treated of as "imido-ethers" on p. 200.

The "official name" of the amides is formed by adding the word "amide" to the name of the hydrocarbon.

Formamide (*Methane-amide*), $HCO.NH_2$, is a liquid readily soluble in water and alcohol, which boils with partial decomposition at about 200°, and breaks up into CO and NH_3 when quickly heated. It yields hydrocyanic acid when heated with P_2O_5.

It unites in molecular proportions with chloral to form the so-called "**chloral-amide,**" which is used as a disinfectant, preservative, and hypnotic.

Acetamide (*Ethane-amide*), $C_2H_3O.NH_2$. Long needles, readily soluble in water and alcohol. M. Pt. 82°, B. Pt. 222°.

Aceto-brom-amide, $C_2H_3O.NHBr$. Colourless rectangular plates.

Di-acetamide, $(C_2H_3O)_2NH$. M. Pt. 78°, B. Pt. 223°. **Tri-acetamide**, $(C_2H_3O)_3N$. See B. **23**, 2394.

The high boiling points of the amides are worthy of notice; they stand in striking contrast to the low boiling points of the amines containing the same number of carbon atoms.

Among the amides of haloid-substitution acids may be mentioned:

Mono-chlor-acetamide, $CH_2Cl—CO.NH_2$, M. Pt. 116°, B. Pt. 225°.

Tri-chlor-acetamide, $CCl_3—CO.NH_2$, M. Pt. 136°, B. Pt. 239°.

For **Isomers of the Amides**, see p. 200.

F. Amido-chlorides and Imido-chlorides.

By the action of PCl_5 upon the primary amides, an exchange of Cl_2 for O takes place, giving rise in the first instance to the so-called amido-chlorides, *e.g.* acet-amido chloride, $CH_3—CCl_2.NH_2$; these are extremely easily decomposable compounds, being reconverted by water into amide and hydrochloric acid, and readily giving up HCl, with formation of imido-chlorides, *e.g.* $CH_3—CCl{=}NH$, acet-imido chloride. The imido-chlorides also decompose easily as a rule, likewise yielding with water the amide and hydrochloric acid. When heated, they break up into nitrile and hydrochloric acid.

The alkylated amides (p. 194) also yield amido-chlorides, *e.g.* $CH_3.CO.NH.C_2H_5$ gives $CH_3.CCl_2.NH.C_2H_5$, ethyl acet-amido chloride, and $CH_3—CO.NR_2$ gives $CH_3—CCl_2.NR_2$; if these still contain amido-hydrogen, they likewise pass readily into imido-chlorides, *e.g.* $CH_3.CCl{=}N.C_2H_5$, ethyl acet-imido chloride.

The chlorine in these compounds is very active, chemically; it can be exchanged for sulphur or for an ammonia (amine-) residue by the action of sulphuretted hydrogen, ammonia, or amine, with the formation of thiamides and amidines, thus:

$$CH_3.CCl_2.NHR + H_2S = CH_3.CS.NHR + 2HCl.$$
$$CH_3.CCl:NR + NH_3 = CH_3.C(NH_2):NR, \text{ etc.}$$

Most of the amido- and imido-chlorides known, (*O. Wallach*, 1875), contain aromatic radicles, *e.g.* C_6H_5, phenyl, and the same remark also applies to the following classes of compounds.

G. Thiamides and Imido-thio-ethers.

Thiamides are compounds derived from the amides by the exchange of oxygen for sulphur, *e.g.* $CH_3.CS.NH_2$, aceto-thiamide or thiacetamide,* $CH_3.CS.NHC_6H_5$, thiacetanilide. They are mostly crystalline compounds, and result from the addition of H_2S to the nitriles, (*Cahours*), *e.g.*:

$$CH_3.CN + H_2S = CH_3.CS.NH_2;$$

by treating acid amides with P_2S_5; from the amido- etc. chlorides, as given above; and by the action of H_2S or CS_2 upon the amidines. Both simple and alkylated thiamides are known.

The thiamides, $R—CS.NH_2$, break up upon heating into nitrile and sulphuretted hydrogen, (see p. 117). They are all easily saponified by alkalies, etc., with formation of the corresponding acid, ammonia (amine) and H_2S, thus:

$$R—CS.NHR + 2H_2O = R—CO.OH + H_2S + NH_2.R.$$

They are rather more acid in character than the amides, and thus many of them are soluble in alkali and yield metallic derivatives. Consequently for them, as well as for the amides, the formula $R—C\begin{smallmatrix}\diagup SH\\ \diagdown NH\end{smallmatrix}$ is taken into consideration (see below; also under the cyanogen compounds, Section F).

The alkylated thiamides of formic acid also result from the addition of hydrogen sulphide to the iso-nitriles:

$$CN.R + H_2S = H—CS.NHR.$$

From such a hypothetical "pseudo-form" of thiacetamide, viz.:

$$CH_3—C\begin{smallmatrix}\diagup SH\\ \diagdown NH,\end{smallmatrix}$$

which one may term acetimido-thio-hydrate, or iso-thiacetamide, there are derived a number of compounds, the *Imido-thio-ethers*, by the replacement of the

* Ethane-thion-amide.

sulphydril, and also of the imido-, hydrogen by an alcohol radicle, *e.g.* acetimido-thio-ethyl, $CH_3-C\leqslant^{S.CH_3}_{NH}$; methyl iso-thio-acetanilide, $CH_3-C\leqslant^{S.CH_3}_{N.C_6H_5}$. They are decomposed by hydrochloric acid into ethers of thiacetic acid, thus:

$$CH_3-C(NH).S.CH_3 + H_2O = CH_3-CO.SCH_3 + NH_3.$$

These imido-thio-ethers are prepared by the action of mercaptans upon nitriles in presence of hydrochloric acid gas (*Pinner*), and by the action of alkyl iodides upon thiamides (*Wallach, Bernthsen*):

$$R.C\leqslant^{S}_{NH_2} + C_2H_5I = R.C\leqslant^{SC_2H_5}_{NH} + HI.$$

Imido-ethers, $R-C\leqslant^{NH}_{OR''}$ which are the oxygen compounds corresponding to the above imido-thio-ethers, and which are isomeric with the amides, are also known, (*Pinner*). They are derived from the imido-hydrates of the acids, *e.g.* from acetimido hydrate, $CH_3-C\leqslant^{NH}_{OH}$, hypothetical compounds unknown in the free state, which are isomeric with the simple amides. The imido-ethers result from the combination of a nitrile with an alcohol under the influence of hydrochloric acid gas, and in certain cases by alkylating amides; some of them are liquids which boil without decomposition, but others are only known in the form of salts.

H. Amidines.

Amidines or amimides are compounds derived from the amides, $R-CO.NH_2$, $R.CO.NHR'$, and $R-CO.NR'_2$, by the exchange of oxygen for the imido-residue NH or $(NR)''$:

$$CH_3-C\leqslant^{NH}_{NH_2} \qquad CH_3-C\leqslant^{NC_6H_5}_{NHC_6H_5}$$

Acetamidine (ethane-amidine). Ethenyl-diphenyl amidine.

The amidines are well characterized and partly crystalline bases which often form stable salts. They differ however from the amines in that they are easily saponified, a property which is common to all acid derivatives.

Formation. (1) By heating the amides with amines in presence of PCl_3 (*Hofmann*):

$$R-CO.NHR' + NH_2R' = R-C(NR')(NHR') + H_2O.$$

(2) By treating the imido-chlorides, thiamides and iso-thiamides with ammonia or with primary or secondary amines (*Wallach*, *Bernthsen*), thus:

$$R—CS.NH_2 + NH_2R' = R—C(NH)(NHR') + H_2S;$$
$$R—C(NH)(SR) + NH_3 = R—C(NH)(NH_2) + RSH.$$

(3) By heating the nitriles with (primary or secondary) amine hydrochlorate; this is a particularly easy method when aromatic amines are used, but not in the case of chloride of ammonium (*Bernthsen*):

$$CH_3—CN + NH_2.R = CH_3—C(NH)(NHR).$$

(4) By the action of amine bases or ammonia upon imido-ethers.

Behaviour. (1) They decompose into ammonia or amine and acid upon boiling with acids or alkalies (see above), and into ammonia and amide upon boiling with water.

(2) In the dry state they easily break up on heating into ammonia or amine and acid nitrile, so long as the imido-hydrogen atom has not been replaced by alcoholic radicle.

(3) Upon heating with hydrogen sulphide, thiamides are formed.

In this reaction combination between the two reagents at first occurs, thus:

$$R—C\begin{cases}NH \\ NH.R\end{cases} + H_2S = R—C\begin{cases}NH_2 \\ SH \\ NH.R'\end{cases}$$

the resulting addition product then breaking up in two directions, viz. (*a*) into $R—CS.NH_2 + NH_2R$, and (*b*) into $R—CS.NHR + NH_3$. Similar intermediate addition compounds must be assumed in corresponding reactions, *e.g.* in the conversion of imido-chlorides into amides.

(4) Upon being heated with CS_2, the amidines also yield thiamides, thiocyanic acid or an iso-thiocyanate being formed at the same time.

Most of the thiamides which have been prepared belong to the aromatic group. (See A. **184**, 129; **192**, 1; B. **12**, 1061.)

Amidoximes.

As amidoximes are designated compounds which result on the addition of hydroxylamine to nitriles, and which, from this mode of formation

and from their properties, appear to be amidines in which an amido-(imido-) hydrogen atom is replaced by hydroxyl :

$$R—CN + NH_2OH = R—C\begin{smallmatrix}\nearrow N.OH \\ \searrow NH_2\end{smallmatrix}.$$

Such an amidoxime is, for instance, **Isuret,*** $H—C\begin{smallmatrix}\nearrow N.OH \\ \searrow NH_2\end{smallmatrix}$, also termed methenyl amidoxime, isomeric with urea, which results from hydrocyanic acid and hydroxylamine; also **Ethenyl amidoxime**, $CH_3—C(N.OH)(NH_2)$. These compounds are decomposed by saponifying agents in a similar way to the amidines. Related to them are substances of the constitution $R—C\begin{smallmatrix}\nearrow N.OH \\ \searrow O.C_2H_5\end{smallmatrix}$, and the hydroxamic acids, *e.g.* benz-hydroxamic acid, $R—C\begin{smallmatrix}\nearrow N.OH \\ \searrow NH_2\end{smallmatrix}$ $(R=C_6H_5)$. (Cf. *Tiemann*, B. **17**, 129, 1685; *Lossen*, B. **17**, 1587.)

The hydroxamic acids show interesting cases of isomerism. (A. **161**, 347; **175**, 271; **186**, 1; **252**, 170; B. **24**, 3447; **25**, 433.)

VIII. POLYATOMIC ALCOHOLS.

A. Diatomic Alcohols or Glycols.

$$C_nH_{2n+2}O_2, = C_nH_{2n}(OH)_2.$$

The diatomic alcohols differ from the monatomic in the same way as the di-acid bases do from the mono-acid. Just as the di-acid bases react with a monobasic acid to form neutral and basic salts, while a mono-acid base can only yield a neutral salt, so do the diatomic alcohols give with monobasic acids two series of ethers, and with ammonia two kinds of amines, etc. Of these compounds the members of the one class correspond to the neutral salts, and possess in full degree the character of ethers, amines, etc., while the members of the other retain their alcoholic character and correspond in composition with the basic salts (which still retain their basic nature), thus:

$Pb\begin{cases}OH \\ OH\end{cases}$	$Pb\begin{cases}OH \\ Cl\end{cases}$	$Pb\begin{cases}Cl \\ Cl\end{cases}$
Lead hydroxide.	Basic lead chloride.	Neutral lead chloride.

* Methane-amidoxime.

	$C_2H_4 \begin{cases} OH \\ Cl \end{cases}$ Glycol chlorhydrin.	$C_2H_4 \begin{cases} Cl \\ Cl \end{cases}$ Glycol dichlorhydrin.
$C_2H_4 \begin{cases} OH \\ OH \end{cases}$ Glycol.	$C_2H_4 \begin{cases} OH \\ O.C_2H_3O \end{cases}$ Glycollic acetate.	$C_2H_4 \begin{cases} O.C_2H_3O \\ O.C_2H_3O \end{cases}$ Glycollic di-acetate.
	$C_2H_4 \begin{cases} OH \\ NH_2 \end{cases}$ Hydroxy-ethylamine.	$C_2H_4 \begin{cases} NH_2 \\ NH_2 \end{cases}$ Ethylene diamine.

The above compounds are therefore alcohols similar to the monatomic, and, like these, they give rise to every class of alcoholic derivative. But when, for example, the formation of an ether such as glycollic acetate has taken place, this still behaves as a monatomic alcohol, yielding, *e.g.* with a second molecule of acid, a new ether; it is therefore termed an ether-alcohol or ester-alcohol.

It is not necessary that both the groups which replace the hydrogen or hydroxyl should be of the same nature; thus we know a mixed derivative of the composition $C_2H_4{<}{}^{NH_2}_{SO_3H}$, which possesses at one and the same time the character of an amine and of a sulphonic acid.

The glycols are mostly thick liquids of sweetish taste, being only occasionally solid crystalline compounds, easily soluble in water and alcohol, but difficultly soluble in ether. Their boiling points are much higher than those of the corresponding monatomic alcohols, just as these latter possess considerably higher boiling points than the hydrocarbons from which they are derived.

Constitution. Just as the monatomic alcohols are characterized by the presence of a hydroxyl group linked to a hydrocarbon radicle, *so in the diatomic alcohols two such hydroxyls* must be assumed; and, as we look upon the monatomic alcohols as oxy-hydrocarbons, so we may regard the diatomic alcohols as di-oxy-hydrocarbons, *i.e.* as being derived from the hydrocarbons by a double replacement of H by OH.

Glycols which would contain two hydroxyls linked to the same carbon atom are incapable of existence, and are only

known in derivatives (see pp. 142 and 152). All glycols contain their hydroxyls attached to two different carbon atoms. Glycol has thus the constitution $CH_2(OH)—CH_2(OH)$, which can be proved directly by transforming it, by means of hydrochloric acid, into glycol chlorhydrin, $CH_2Cl—CH_2.OH$, and oxidizing the latter to mono-chloracetic acid, $CH_2Cl—CO.OH$. In this last compound the chlorine and hydroxyl are bound to different carbon atoms, and consequently the same applies to glycol chlorhydrin and to glycol. (Cf. p. 76.)

The monatomic alcohols are distinguished as primary, secondary, and tertiary. The glycols may in the same way be characterized as di-primary when they contain the group $CH_2.OH$ twice, as in glycol; as primary-secondary when they contain the group $CH_2.OH$ together with the group CH.OH, as in propylene glycol, $CH_3—CH(OH)—CH_2OH$; further as di-secondary, primary-tertiary, secondary-tertiary, and di-tertiary. In all these cases the behaviour of the compound upon oxidation yields an explanation of its nature. (For particulars, (see p. 219 *et seq.*)

Modes of formation. 1. From the di-bromo-substitution products of the hydrocarbons, *e.g.* ethylene bromide:

(*a*) By transformation into the di-acetic ether, by means of silver or potassium acetate, and saponification of the ether so produced by potash or baryta water:

$$\underbrace{C_2H_4Br_2}_{\text{Ethylene bromide.}} + 2AgC_2H_3O_2 = \underbrace{C_2H_4(C_2H_3O_2)_2}_{\text{Glycollic di-acetate.}} + 2AgBr;$$

$$C_2H_4(C_2H_3O_2)_2 + 2KOH = C_2H_4(OH)_2 + 2C_2H_3O_2K.$$

In the actual preparation of glycol from ethylene bromide, potassium acetate and strong alcohol (*Demole*), this saponification ensues directly upon prolonged boiling of the mixture.

(*b*) By boiling with water and lead oxide or potassium carbonate, by which means the acid produced is taken up, and so the reaction is facilitated:

$$C_2H_4Br_2 + 2HOH = C_2H_4(OH)_2 + 2HBr.$$

2. By the reduction of ketones to secondary alcohols, the so-called

pinacones, *i.e.* di-tertiary glycols, result as bye-products, (see pp. 86 and 207), thus:

$$(CH_3)_2CO + CO(CH_3)_2 + H_2 = \underbrace{(CH_3)_2{=}C(OH){-}C(OH){=}(CH_3)_2}_{\text{Pinacone}}.$$

3. By the combination of olefines with H_2O_2, or from their oxidation by means of $KMnO_4$, the glycols are produced directly, and by their combination with ClOH, the chlorhydrins:

$$C_2H_4 + ClOH = C_2H_4Cl(OH).$$

Behaviour. 1. As in the case of the monatomic alcohols, the hydrogen is directly replaceable by potassium or sodium, with the formation of alcoholates, *e.g.* $C_2H_4{<}^{OH}_{ONa}$, and $C_2H_4{<}^{ONa}_{ONa}$, sodium and di-sodium glycols.

2. The metal in these compounds may be exchanged for new alcohol radicle by treatment with alkyl iodide, with formation of glycollic ethers:

$$C_2H_4(ONa)_2 + 2C_2H_5I = 2NaI + \underbrace{C_2H_4(O.C_2H_5)_2}_{\text{Ethylene di-ethyl ether}}.$$

These ethers, like those of the monatomic alcohols, are stable against saponifying agents.

3. Acids act upon them to produce ethers, which are either neutral ethers or ether-alcohols (see p. 202).

The halogen ethers of the glycols are termed chlor-, brom-, or iodhydrins, *e.g.* glycol chlorhydrin, $C_2H_4Cl(OH)$, glycol di-chlorhydrin, $C_2H_4Cl_2$, etc. The ether-alcohols which result from the action of halogen hydride may also be regarded as mono-substitution products of the monatomic alcohols, which cannot be prepared directly, *e.g.* $C_2H_4Cl(OH)$, monochlor-ethyl alcohol. Similarly the neutral halogen hydride ethers, $C_2H_4Cl_2$, $C_2H_4Br_2$, etc., are nothing else than the di-substitution products of the paraffins.

4. The chlor-, brom-, and iodhydrins, as the chlorides, etc. of the monatomic alcohols, constitute the bridge for the preparation of most of the other glycol derivatives; thus they yield thio-glycols with potassium hydrosulphide, glycollic amines with ammonia, glycollic sulphonic acids with bisulphite of soda, etc.

5. By the splitting off of HCl from ethylene chlorhydrin by means of alkali, there is formed an anhydride of glycol, ethylene oxide, $\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array} \!\!>\! O$, (see p. 208), homologues of which have also been prepared.

6. The glycols frequently yield aldehydes or ketones by giving up water, for instance, ethylene glycol is converted into aldehyde by warming with chloride of zinc, or with water to 230°. This reaction is explained by assuming the intermediate formation of unsaturated alcohols which are not in themselves capable of existence, *e.g.* $CH_2{=}CH(OH)$, but which immediately undergo transformation into the isomeric aldehydes or ketones.

7. For the oxidation products of glycol, see above, also p. 219.

Methylene- and Ethylidene glycols. See Aldehydes.

Ethylene glycol,* *glycol*, $C_2H_4(OH)_2$, (*Wurtz*, A. **100**, 110). Is prepared from ethylene bromide by means of potassium acetate in alcoholic solution (*Demole*), or of potassium carbonate in aqueous solution, as given above, (A. **192**, 250). For properties, see above. Its formula has been corroborated by the determination of its vapour density. Oxidizing agents transform it into glycollic and oxalic acids.

Propylene glycol is known in two isomeric forms, viz. :

(*a*) **Tri-methylene glycol†** or **β-Propylene glycol,** $CH_2(OH)$—CH_2—CH_2OH, which is prepared from tri-methylene bromide, and is a di-primary glycol; B. Pt. 216°. It is also produced by the schizomycetes fermentation of glycerine, (B. **14**, 2270).

(*b*) **α-Propylene glycol,‡** CH_3—$CH(OH)$—$CH_2(OH)$, can be prepared from propylene bromide in an analogous manner, but is most easily got by distilling glycerine with caustic soda. B. Pt. 188°. Becomes optically (—) active on fermentation, *i.e.* fission fungi convert it into two active modifications (+ and —), the former of which is more readily attacked by fermentation than the latter.

Four Butylene glycols, and various Amylene- and Hexylene- glycols, etc., are also known. Among them, the γ-glycols (in which both the hydroxyls are in the γ-position, and which therefore contain the group —C(OH)—C_α—C_β—C_γ(OH)—), yield compounds of the furfurane series by the

* 1.2-Ethane-diol. † 1.3-Propane-diol. ‡ 1.2-Propane-diol.

formation of anhydride (B. **22**, 2567), and therefore stand in close relation to thiophene and pyrrol.

Pinacone or **Tetramethyl-ethylene glycol** (2-3-*Dimethyl*-2-3-*Butane-diol*), $(CH_3)_2=C(OH)-C(OH)=(CH_3)_2$. For formation see p. 205. Its hydrate, $(+6H_2O)$, forms large quadratic tables; in the anyhydrous state it is a crystalline mass melting at 38° and boiling at 172°. When warmed with dilute sulphuric acid it yields pinacoline, $CH_3-CO-C\equiv(CH_3)_3$ (see p. 157).

Derivatives of the Glycols.

Ethyl ethers. **Glycol ethyl ether,** $C_2H_4<^{OH}_{O.C_2H_5}$, and **Glycol di-ethyl ether,** $C_2H_4(O.C_2H_5)_2$, are liquids of pleasant ethereal odour, boiling at about 70° lower than glycol.

Acid derivatives. **Glycollic acetate,** $C_2H_4<^{OH}_{O.C_2H_3O}$, and **Glycollic di-acetate,** $C_2H_4(O.C_2H_3O)_2$, are liquids easily soluble in water, which boil at a slightly lower temperature than glycol. The former is converted by gaseous hydrochloric acid into glycol chlor-acetin, $C_2H_4<^{Cl}_{O.C_2H_3O}$, which may also be regarded as chlorinated ethyl acetate.

Glycol chlorhydrin, $C_2H_4.Cl.OH$, is obtained by passing hydrochloric acid gas into warm glycol, (B. **16**, 1407), or by the direct combination of ethylene and hypochlorous acid. It is a liquid miscible with water, and boiling at 130°, differing in this point from its corresponding alcohol to almost the same extent as ethyl chloride does from alcohol.

Glycol bromhydrin, $C_2H_4.Br.OH$, and **Glycol iodhydrin,** $C_2H_4.I.OH$, are analogous compounds; the last named decomposes upon distillation.

Sulphuric ethers of glycol, *e.g.* **Glycol-suphuric acid,** $C_2H_4<^{OH}_{O.SO_3H}$, also exist. The latter is similar to ethyl-sulphuric acid in its behaviour.

Glycollic di-nitrate, $C_2H_4(NO_3)_2$, is prepared by acting on glycol with sulphuric and nitric acids:

$$C_2H_4(OH)_2 + 2NO_2OH = C_2H_4(O.NO_2)_2 + 2H_2O.$$

It is a yellowish liquid, insoluble in water, which is saponified by alkalies and explodes on being heated. The formation of such nitric ethers is characteristic of the poly-atomic alcohols, (see glycerine, p. 216).

By treating ethylene bromide with potassium cyanide, **ethylene cyanide,** $C_2H_4(CN)_2$, is obtained. It is crystalline, and goes into succinic acid, $C_2H_4(CO_2H)_2$, on saponification,

5. By the splitting off of HCl from ethylene chlorhydrin by means of alkali, there is formed an anhydride of glycol, ethylene oxide, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \!\!>\! O$, (see p. 208), homologues of which have also been prepared.

6. The glycols frequently yield aldehydes or ketones by giving up water, for instance, ethylene glycol is converted into aldehyde by warming with chloride of zinc, or with water to 230°. This reaction is explained by assuming the intermediate formation of unsaturated alcohols which are not in themselves capable of existence, *e.g.* $CH_2{=}CH(OH)$, but which immediately undergo transformation into the isomeric aldehydes or ketones.

7. For the oxidation products of glycol, see above, also p. 219.

Methylene- and Ethylidene glycols. See Aldehydes.

Ethylene glycol,* *glycol*, $C_2H_4(OH)_2$, (*Wurtz*, A. **100**, 110). Is prepared from ethylene bromide by means of potassium acetate in alcoholic solution (*Demole*), or of potassium carbonate in aqueous solution, as given above, (A. **192**, 250). For properties, see above. Its formula has been corroborated by the determination of its vapour density. Oxidizing agents transform it into glycollic and oxalic acids.

Propylene glycol is known in two isomeric forms, viz.:

(*a*) **Tri-methylene glycol†** or **β-Propylene glycol**, $CH_2(OH)$—CH_2—CH_2OH, which is prepared from tri-methylene bromide, and is a di-primary glycol; B. Pt. 216°. It is also produced by the schizomycetes fermentation of glycerine, (B. **14**, 2270).

(*b*) α-**Propylene glycol,‡** CH_3—$CH(OH)$—$CH_2(OH)$, can be prepared from propylene bromide in an analogous manner, but is most easily got by distilling glycerine with caustic soda. B. Pt. 188°. Becomes optically (—) active on fermentation, *i.e.* fission fungi convert it into two active modifications (+ and —), the former of which is more readily attacked by fermentation than the latter.

Four **Butylene glycols**, and various **Amylene-** and **Hexylene- glycols**, etc., are also known. Among them, the γ-glycols (in which both the hydroxyls are in the γ-position, and which therefore contain the group —C(OH)—C—C—C(OH)—), yield compounds of the furfurane series by the
α β γ

* 1-2-Ethane-diol. † 1-3-Propane-diol. ‡ 1-2-Propane-diol.

formation of anhydride (B. **22**, 2567), and therefore stand in close relation to thiophene and pyrrol.

Pinacone or **Tetramethyl-ethylene glycol** (2·3-*Dimethyl*-2·3-*Butane-diol*), $(CH_3)_2{=}C(OH)-C(OH){=}(CH_3)_2$. For formation see p. 205. Its hydrate, $(+6H_2O)$, forms large quadratic tables; in the anyhydrous state it is a crystalline mass melting at 38° and boiling at 172°. When warmed with dilute sulphuric acid it yields pinacoline, $CH_3{-}CO{-}C{\equiv}(CH_3)_3$ (see p. 157).

Derivatives of the Glycols.

Ethyl ethers. **Glycol ethyl ether**, $C_2H_4{<}^{OH}_{O.C_2H_5}$, and **Glycol di-ethyl ether**, $C_2H_4(O.C_2H_5)_2$, are liquids of pleasant ethereal odour, boiling at about 70° lower than glycol.

Acid derivatives. **Glycollic acetate**, $C_2H_4{<}^{OH}_{O.C_2H_3O}$, and **Glycollic di-acetate**, $C_2H_4(O.C_2H_3O)_2$, are liquids easily soluble in water, which boil at a slightly lower temperature than glycol. The former is converted by gaseous hydrochloric acid into glycol chlor-acetin, $C_2H_4{<}^{Cl}_{O.C_2H_3O}$, which may also be regarded as chlorinated ethyl acetate.

Glycol chlorhydrin, $C_2H_4.Cl.OH$, is obtained by passing hydrochloric acid gas into warm glycol, (B. **16**, 1407), or by the direct combination of ethylene and hypochlorous acid. It is a liquid miscible with water, and boiling at 130°, differing in this point from its corresponding alcohol to almost the same extent as ethyl chloride does from alcohol.

Glycol bromhydrin, $C_2H_4.Br.OH$, and **Glycol iodhydrin**, $C_2H_4.I.OH$, are analogous compounds; the last named decomposes upon distillation.

Sulphuric ethers of glycol, *e.g.* **Glycol-suphuric acid**, $C_2H_4{<}^{OH}_{O.SO_3H}$, also exist. The latter is similar to ethyl-sulphuric acid in its behaviour.

Glycollic di-nitrate, $C_2H_4(NO_3)_2$, is prepared by acting on glycol with sulphuric and nitric acids:

$$C_2H_4(OH)_2 + 2NO_2OH = C_2H_4(O.NO_2)_2 + 2H_2O.$$

It is a yellowish liquid, insoluble in water, which is saponified by alkalies and explodes on being heated. The formation of such nitric ethers is characteristic of the poly-atomic alcohols, (see glycerine, p. 216).

By treating ethylene bromide with potassium cyanide, **ethylene cyanide**, $C_2H_4(CN)_2$, is obtained. It is crystalline, and goes into succinic acid, $C_2H_4(CO_2H)_2$, on saponification,

whence it may be termed the nitrile of this acid. Nascent hydrogen transforms it into butylene diamine, $C_4H_8(NH_2)_2$, (see p. 210). Similarly ethylene chlorhydrin is converted by potassium cyanide into the HCN-derivative of glycol,

Ethylene cyanhydrin,* $CH_2(OH)—CH_2.CN$, which also possesses the properties of an acid nitrile, (see lactic acid). Isomeric with it is **ethylidene cyanhydrin,** $CH_3.CH(OH)—CN$, the addition product of hydrocyanic acid with aldehyde, (p. 144).

Acetone cyanhydrin, $(CH_3)_2{=}C(OH)—CN$, see p. 155.

The anhydride, **Ethylene oxide,** C_2H_4O, (*Wurtz*), is obtained by distilling glycol chlorhydrin with caustic potash solution. It is a mobile liquid of ethereal odour, mixing and gradually combining with water to ethylene glycol. B. Pt. 13·5° ; Sp. Gr. < 1. It also combines with acids to chlorhydrins or mono-ethers of the glycols, this affinity for acids being so strong as to give it a well marked basic character, which is further shown by its precipitating the hydrates of the heavy metals from solutions of their salts. It is isomeric with aldehyde.

Ethylene oxide combines with glycol to form the so-called Polyglycols, *e.g.* **Di-ethylene glycol,** $C_2H_4(OH)—O—C_2H_4(OH)$.

Mercaptans and sulphides of the glycol series also exist, *e.g.* **Glycol mercaptan,**† $C_2H_4(SH)_2$, **Ethylene mono-thio-hydrate,** $C_2H_4(OH)(SH)$, and **Di-ethylene di-sulphide,** $(C_2H_4)_2S_2$, the last of which forms a sulph-oxide and a sulphone. **Thio-di-glycollic chloride,** $S(C_2H_4Cl)_2$, is an extremely poisonous liquid.

Amines of the Diatomic Alcohols.

These are derived from glycol by the replacement of one or two hydroxyl groups by amidogen :

$$C_2H_4\begin{cases}OH\\NH_2\end{cases} \qquad\qquad C_2H_4\begin{cases}NH_2\\NH_2\end{cases}$$

Oxy-ethylamine. Ethylene diamine.

In the former case monatomic (primary) amines containing oxygen result, compounds which retain at the same time their

* 3-Propanol-nitrile. † 1-2-Ethane-dithiol.

alcoholic character; in the latter, diatomic (primary) bases free from oxygen, the diamines, which are in every respect analogous to ethylamine. These compounds may also of course be held as being derived from one or two molecules of ammonia by the exchange of H for $(C_2H_4.OH)$, "oxy-ethyl," or of H_2 for (C_2H_4), thus:

$$N\begin{cases}H\\H\\C_2H_4.OH\end{cases} \qquad N_2\begin{cases}H_2\\H_2\\(C_2H_4)''\end{cases}$$

This latter view permits of the prediction of secondary and tertiary bases, *e.g.*

$$N\begin{cases}H\\(C_2H_4.OH)_2\end{cases} \quad \text{and} \quad N(C_2H_4.OH)_3$$

$$N_2\begin{cases}H_2\\(C_2H_4)''_2\end{cases} \quad \text{and} \quad N_2(C_2H_4)''_3;$$

and also of quarternary ammonium bases, of such, among others, as still contain monatomic alcohol radicles, *e.g.*:

$$N\begin{cases}(CH_3)_3\\(C_2H_4.OH),\ \text{Choline.}\\OH\end{cases}$$

Such bases actually exist, and show, according to their constitution, the behaviour of primary, secondary, etc., amines or ammonium bases. Ethylene diamine, for instance, can react not only with ethylene bromide, but also with the halogen compounds of the monatomic alcohol radicles.

The bases containing oxygen, such as oxy-ethylamine, etc., are termed **Oxy-alkyl-bases** or **Hydramines**, and, by *Ladenburg*, **Alkines** (B. **22**, 2583); the carbinol-group, $\equiv C(OH)$, he designates here "Alkine," and (*e.g.*) the compound $N(CH_3)_2-CH_2-CH_2(OH)$, "trimethyline-alkyl."

If two hydrogen atoms in a molecule of ammonia are replaced by a divalent alcohol radicle, "**Imines**" result, *e.g.* pentamethylene-imine, $(C_5H_{10})''NH$ (see Piperidine).

Their *Modes of formation* are likewise for the most part analogous to those of the monatomic alcohol bases, viz.:

(1) By heating ethylene bromide, etc., with alcoholic ammonia to 100° (*Hofmann*).

$$C_2H_4Br_2+2NH_3 = C_2H_4(NH_2)_2+2\,HBr;$$
$$C_2H_4(NH_2)_2+C_2H_4Br_2 = (C_2H_4)_2N_2H_2+2HBr.$$

The primary, secondary and tertiary bases, which are formed simultaneously, can be separated by fractional distillation.

The oxy-alkyl bases are obtained in an analogous manner by using ethylene chlorhydrin, thus:

$$C_2H_4(OH)Cl + NH_3 = C_2H_4(OH)(NH_2) + HCl.$$

In this case also primary, secondary and tertiary bases are produced at the same time, and are separated by the fractional crystallization either of their HCl salts or of their double platinum chlorides.

Ethylene chlorhydrin yields choline hydrochlorate with tri-methylamine.

(2) Primary diamines result from the reduction of the nitriles, $C_nH_{2n}(CN)_2$, which is best effected by metallic sodium in the hot alcoholic solution:

$$\underbrace{C_2H_4(CN)_2}_{\text{Ethylene cyanide.}} + 4H_2 = C_2H_4(CH_2.NH_2)_2, = \underbrace{C_4H_8(NH_2)_2}_{\text{Butylene diamine.}}$$

(3) Hydramines ensue by the direct combination of ammonia with 1, 2, or 3 molecules of ethylene oxide (*Wurtz*), thus:

$$C_2H_4O + NH_3 = C_2H_4(OH)(NH_2).$$

Ethylene oxide, tri-methylamine and water combine to choline:

$$C_2H_4O + H_2O + N(CH_3)_3 = C_2H_4(OH)[N(CH_3)_3.OH].$$

Ethylene diamine, $C_2H_4(NH_2)_2$, **Di-ethylene diamine**, $(C_2H_4)_2N_2H_2$, etc., are colourless liquids distilling without decomposition. The former boils at 123°, and has an ammoniacal odour; the latter melts at 104° and boils at 146°, and is identical with piperazine, *i.e.* hexahydro-pyrazine. Hence it possesses the constitutional formula $C_2H_4\langle{}^{NH}_{NH}\rangle C_2H_4$, and has a ring-shaped atomic linking (*Hofmann*, B. **23**, 3297).

Tri-methylene diamine, $C_3H_6(NH_2)_2$ (see B. **17**, 1789). By the loss of NH_3, it yields **Trimethylene-imine** (*Propane-imine*), $C_3H_6{=}NH$, a liquid resembling piperidine (B. **23**, 2727).

Tetramethylene-diamine (*1-4-Butane-diamine*), *putrescine*, *butylene-diamine*, $CH_2(NH_2){-}CH_2{-}CH_2{-}CH_2(NH_2)$, is prepared according to method 2, and also results (*e.g.*) from the putrefaction of flesh. As a "γ-diamine," *i.e.* the diamine of a γ-glycol (p. 206), it is nearly related to pyrrol, from which it is formed by the action of hydroxylamine (whereby a dioxime is first produced), and subsequent reduction (B. **22**, 1968).

Penta-methylene diamine, *cadaverine*, $C_5H_{10}(NH_2)_2 = CH_2(NH_2){-}(CH_3)_3{-}CH_2(NH_2)$, is formed by the reduction of tri-methylene cyanide, $CN{-}(CH_2)_3{-}CN$, which on its part is prepared from tri-methylene bromide, $CH_2Br{-}CH_2{-}CH_2Br$, and KCN (*Ladenburg*). It is a colourless syrupy liquid of very pronounced spermaceti and piperidine odour, which solidifies in the cold, and boils at 178°–179°. It possesses

especial interest, because, being a δ-diamine, it gives up ammonia and yields piperidine, $C_5H_{11}N$, synthetically.

Oxy-ethylamine (1-2-*Ethanol-amine*) and the other hydramines are colourless bases which decompose on distillation (cf. *Knorr*, B. **22**, 2081).

Bromo-ethylamine, $CH_2Br-CH_2.NH_2$, is the bromhydrin corresponding to the "alcohol" oxy-ethylamine. It is of use for synthetic reactions (B. **21**, 566; **22**, 1139).

For **δ-chloro butylamine** and **ε-chloro-amylamine**, see B. **24**, 3231; **25**, 415.

Choline, *bilineurine*, *ethylol-trimethyl-ammonium hydroxide*, $N(CH_3)_3.(C_2H_4.OH)(OH)$ or $C_2H_4{<}^{OH}_{N(CH_3)_3.OH}$ (*Strecker*), is found in the bile (χολή, bile), brain, yolk of egg, etc., being present in these combined with fatty acids and glycerine-phosphoric acid as lecithine. It is also found in herring brine, hops, beer, and in many fungi, etc., and is obtained by boiling sinapine with alkalies (the old name for this product was "Sincaline"). Choline is a strong base, difficultly crystallizable, deliquescent, and absorbing carbonic acid from the air with avidity. It is not poisonous. The HCl salt has the formula $N(CH_3)_3(C_2H_4OH)Cl$. Concentrated HNO_3 oxidizes choline to **Muscarine**, $C_5H_{15}NO_3$ (perhaps $\left(\begin{array}{l}CH(OH)_2\\ | \\ CH_2-N(CH_3)_3.OH\end{array}\right)$, an excessively poisonous base, which is present in toad-stool, *Agaricus muscarius*.

By transforming choline, by means of hydriodic acid, into its iodide, $N(CH_3)_3(C_2H_4I)I$, and treating the latter with moist oxide of silver, and also from the putrefaction of choline, there results:—

Neurine (νεῦρον, nerve), *trimethyl-vinyl-ammonium hydroxide*, $N(CH_3)_3(C_2H_3)OH$ (*Hofmann*). This base, containing the unsaturated radicle "vinyl," C_2H_3, is very similar to choline, and can also be prepared from brain substance; it is only known in solution, and is very poisonous. It can be re-transformed into choline. (For this, and also for derivatives, see *e.g.* A. 267, 249; 268.) Many of these polyvalent bases are found in decaying albumen and in corpses, and are designated **Ptomaïnes** or **Toxines** (cf. *e.g.* B. 19, 2585; also the section *Albuminous Substances*).

Sulphuric and Sulphurous Acid Derivatives of Glycol.

Methylene di-sulphonic acid, *methionic acid*, $CH_2=(SO_3H)_2$; needles. **Oxy-methyl-sulphonic acid**, $CH_2(OH)SO_3H$; difficultly crystallizable. **Ethylene di-sulphonic acid**, $C_2H_4(SO_3H)_2$; a thick liquid.

Oxy-ethyl-sulphonic or isethionic acid, $CH_2(OH)-CH_2(SO_3H)$, and **Ethionic acid,** $CH_2(OSO_3H)—CH_2(SO_3H)$. By treating alcohol with sulphuric anhydride, or by the direct combination of the latter with ethylene, **Carbyl sulphate,** $C_2H_4S_2O_6$, the anhydride of ethionic acid, is formed. It is crystalline and hygroscopic, combining immediately with water to ethionic acid. The latter is easily converted into sulphuric and isethionic acids upon boiling with water. Isethionic acid is isomeric with ethyl-sulphuric, but differs from it sharply in not being saponifiable. It is also produced by the oxidation of ethylene thio-hydrate, $CH_2(OH).CH_2SH$, by nitric acid, and by heating ethylene chlorhydrin with K_2SO_3; it is therefore a sulphonic acid (see p. 115)

Ethionic acid is a sulphuric ether of isethionic acid, in which the latter acts as an alcohol, corresponding with the constitutional formula: $CH_2(O.SO_3H)—CH_2(SO_3H)$.

Isethionic acid is a thick liquid which may solidify to a stellate crystalline mass, and forms stable salts and also an ethyl ether, etc. It yields with PCl_5 the chloride $C_2H_4.Cl—SO_2.Cl$, which decomposes with water to **Chloro-ethyl-sulphonic acid,** $CH_2Cl—CH_2(SO_3H)$. This latter reacts with ammonia (*Kolbe*) to form

Taurine, $C_2H_7NSO_3$ (*Gmelin*), which is present in combination with cholic acid as taurocholic acid in the bile of oxen and many other animals, also in the kidneys, lungs, etc. It crystallizes in large monoclinic prisms, is easily soluble in hot water but insoluble in alcohol, and decomposes upon being strongly heated. From the above mode of formation, it has the constitution $\begin{array}{l}CH_2.NH_2\\ | \\ CH_2.SO_3H\end{array}$ = Amido-ethyl-sulphonic acid, and in accordance with this constitution it unites in itself the properties of an alcoholic amine and a sulphonic acid, and is therefore at the same time a base and an acid. It forms unstable salts with alkalies, but not with acids, the groups NH_2 and SO_3H in the molecule practically neutralizing one another, so that its reaction is neutral. Nitrous acid converts

it into isethionic acid, a reaction analogous to the decomposition of the primary amines by this reagent. As the sulphonic acid of an alcohol, it is not changed by boiling with alkalies and acids.

B. Triatomic Alcohols.

Those alcohols are triatomic which are capable of forming three series of ethers with a monobasic acid, in such manner that the production of the neutral ether requires three molecules of the acid. Three hydroxyls must be assumed in them, so that their chemical behaviour depends upon whether one or two or all three of these are brought into reaction, with the formation of simple and compound ethers, amines, etc.

Thus there exist, for instance, the following three glycerine ethers of acetic acid:

$$C_3H_5\begin{cases}(OH)_2\\ O.C_2H_3O\end{cases} \qquad C_3H_5\begin{cases}OH\\ (O.C_2H_3O)_2\end{cases} \qquad C_3H_5(O.C_2H_3O)_3.$$

Mono-acetin. Di-acetin. Tri-acetin.

Compounds are also known, as in the case of the diatomic alcohols, which contain several different substituents in the place of the hydroxyl.

The triatomic alcohols are colourless thick liquids of sweet taste and high boiling point, and are for the most part easily soluble in water.

Triatomic alcohols with one or two carbon atoms are unknown, in accordance with what has already been said on pp. 142 and 203; one carbon atom binds therefore only one hydroxyl.

Thus the compound $CH(OH)_3$ is incapable of existence, but we know its derivatives ortho-formic ether (p. 163), and **Formyl-tri-sulphonic**

acid, $CH(SO_3H)_3$, a compound resulting from the action of fuming sulphuric acid upon calcium methyl-sulphonate and, like other sulphonic acids, not saponifiable.

Ortho-acetic ether, $CH_3—C(OC_2H_5)_3$ (liquid, B. Pt. 142°), and its isomer, **Ethenyl tri-ethyl ether**, are also derivatives of non-existing tri-hydroxylic compounds.

Glycerine (*Propane-triol*), *propenyl alcohol*, "*Oelsüss*," $C_3H_5(OH)_3$. (*Scheele*, 1779; formula established by *Pelouze* in 1836, and constitution by *Berthelot* and *Wurtz*.)

Synthesis. By heating glyceryl tri-chloride, $C_3H_5Cl_3$ (p. 78), with water to 170°;

$$CH_2Cl\text{-}CHCl\text{-}CH_2Cl + 3H_2O = CH_2(OH)\text{-}CH(OH)\text{-}CH_2(OH) + 3HCl.$$

Glyceryl trichloride is itself obtainable from iso-propyl iodide (which can also be prepared synthetically), by conversion into propylene, addition of Cl_2, and heating the propylene dichloride formed with chloride of iodine (*Friedel* and *Silva*, Bull. Soc. Chim. **20**, 98):

$$C_3H_6Cl_2 + Cl_2 = C_3H_5Cl_3 + HCl.$$

The *constitution* of glycerine follows from this synthesis and also from its relation to tartronic acid (p. 257); each of the three hydroxyls is attached to a separate carbon atom.

Glycerine is also produced by the oxidation of allyl alcohol with permanganate of potash.

Preparation. Glycerine is prepared by saponifying the natural fats and oils, especially olive oil, either by means of superheated steam, or by heating with lime and water, or with sulphuric acid. These are thus broken up into their components, the glycerine distilling over with the superheated steam, and being at the same time purified by means of animal charcoal.

In the manufacture of stearic acid (p. 177), the fats are saponified by sulphuric acid, whereby the glycerine is converted into glyceryl-sulphuric acid, $C_3H_5(OH)_2(O.SO_3H)$, *from which it can be obtained by* boiling with water or with lime. In the preparation of plaister, by boiling fats with lead oxide and water, as at p. 177, an aqueous solution of glycerine is got along with the insoluble lead plaister.

Properties. Thick colourless syrup. Sp. Gr. 1·27. Solidifies, when strongly cooled, to crystals like those of sugar candy,

which melt at 20°. Boils at 290°, but, when impure, it can be distilled without decomposition only under diminished pressure. Very hygroscopic and miscible with water and alcohol in all proportions, but insoluble in ether.

Uses. In the manufacture of liqueurs, fruit preserves, wine, etc.; for non-drying stamp colours and blacking; when mixed with glue, in book printing; as a healing ointment for external use; but especially in the manufacture of nitro-glycerine, and in the colour industry.

Behaviour. 1. It forms with alkalies and other metallic hydroxides soluble alcoholates which readily break up again into their components.

2. By exchanging the typical hydrogen atom for alkyl, it yields ethers, *e.g.* **Mono-ethylin**, $C_3H_5(OH)_2(OC_2H_5)$, and **Tri-ethylin**, $C_3H_5(OC_2H_5)_3$, liquids which boil without decomposition.

3. As an alcohol it forms the most various ethers, thus, with sulphuric acid, the easily saponifiable glyceryl-sulphuric acid, $C_3H_5(OH)_2(O.SO_3H)$; with phosphoric acid, glyceryl-phosphoric acid, $C_3H_5(OH)_2(O.PO_3H_2)$; with nitric acid, nitro-glycerine, $C_3H_5(O.NO_2)_3$; with hydrochloric acid the chlorhydrins, and with the higher fatty acids the fats. For its behaviour with hydriodic acid, or iodine and phosphorus, see p. 74.

4. It yields compounds of a mercaptan or aminic character by exchange of OH for SH or NH_2.

5. By the separation of 2 mols. H_2O, it yields acrolein (see p. 149), and by the indirect separation of 1 mol. H_2O, glycidic alcohol or glycide, $C_3H_6O_2$.

6. Oxidizing agents convert it, according to circumstances, either into glyceric, tartronic, oxalic, tartaric, hydrocyanic, acetic, or formic acid. Halogens oxidize and do not substitute.

7. It yields normal butyl alcohol, caproic acid and butyric acid by certain fission-fungus fermentations. (Cf. B. 16, 844.)

Derivatives.

Chlorhydrins (hydrochloric ethers). By the action of HCl, **Mono-** and **Di-chlorhydrins** result, and by the action of PCl_5 upon these, **Tri-chlorhydrin.** Each of the two first-named exists in two isomeric modifications.

α-Mono-chlorhydrin,* $CH_2(OH)—CH(OH)—CH_2Cl$, is formed from epichlorhydrin, $C_3H_5O.Cl$, and water; **α-Di-chlorhydrin**, $CH_2Cl—CH(OH)—CH_2Cl$, from epichlorhydrin and HCl; **β-Mono-chlorhydrin**, $CH_2(OH)—CHCl—CH_2(OH)$, and **β-Di-chlorhydrin**, $CH_2(OH)—CHCl—CH_2Cl$, by the addition of ClOH to allyl alcohol or allyl chloride.

The chlorhydrins are liquids more or less easily soluble in water, and easily soluble in alcohol and ether, which boil at a lower temperature than glycerine. They may also be regarded as chlorinated propylene glycols or propyl alcohols, (tri-chlorhydrin, $C_3H_5Cl_3$, as trichloro-propane), being transformed by backward substitution into the corresponding alcohols or propane.

Iodhydrins. Mono- and Di-iodhydrin are known, but not Tri-iodhydrin, (see pp. 74 and 72).

Glycide compounds. By the elimination of water from glycerine a compound is obtained which unites within itself the properties of ethylene oxide and of a monatomic alcohol, viz.:

$$\textbf{Glycide alcohol, } C_3H_5O.OH, = CH_2\overset{O}{\frown}CH—CH_2.OH.$$

It may be prepared *e.g.* by the abstraction of HCl from α-mono-chlorhydrin, by means of baryta, just as ethylene chlorhydrin yields ethylene oxide. It is a colourless liquid boiling at 162°, and miscible with water, alcohol and ether, which recombines with H_2O to glycerine and with HCl to chlorhydrin, and, as an alcohol, forms ethers (glycide ethers), etc. It reduces an ammoniacal silver solution. Is isomeric with propionic acid. Its hydrochloric ether is

Epichlorhydrin, $C_3H_5O.Cl$, isomeric with chlor-acetone and propionyl chloride, a mobile liquid of chloroform odour, boiling at 117°, which is formed by the separation of HCl from either of the di-chlorhydrins, and is capable of recombining with H_2O, HCl, etc.

Ethers of Nitric acid. Mono-nitrin, $C_3H_5(OH)_2(O.NO_2)$, **and Tri-nitrin or Nitro-glycerine**, $C_3H_5(O.NO_2)_3$, **are known. The latter is prepared by treating glycerine with a cold mixture of concentrated nitric and sulphuric acids. It is a colourless oil, insoluble in water, poisonous, and of a sweet burning aromatic taste. Sp. Gr. 1·6. M. Pt. about 11°–12°. It burns without explosion, but explodes with terrible violence when quickly heated or when struck, (*Nobel's* explosive oil).**

* 3-Chloro-1,2-Propane-diol

When mixed with kieselguhr in the proportion of 3 parts to 1, it forms dynamite, (*Nobel*, 1867), which is exploded by fulminate of mercury with frightful force. It is saponified by alkalies and by sulphide of ammonium.

Ethers of Organic acids. Mono-formin, $C_3H_5(OH)_2(O.CHO)$, already mentioned at p. 168, is an oily, easily saponifiable liquid, which yields allyl alcohol upon heating.

The **Acetins** are high-boiling liquids soluble in water and ether, which can be prepared synthetically, and which are used technically for the solution of colours for printing.

Mono-, Di-, and Tri-palmitin, $C_3H_5(OH)_2(O.C_{16}H_{31}O)$, etc., can likewise be obtained by synthesis, and melt respectively at 58°, 59°, and 66°. **Tri-palmitin,** $C_3H_5(O.C_{16}H_{31}O)_3$, may be prepared from palm oil (p. 176), and forms glancing mother-of-pearl plates; **Tri-stearin,** $C_3H_5(O.C_{18}H_{35}O)_3$, from mutton tallow or shea butter, M. Pt. 72°; **Tri-oleïn,** $C_3H_5(O.C_{18}H_{33}O)_3$, the chief constituent of olive oil, is an oil which only solidifies at −6°. For the animal and vegetable fats and oils, see p. 176.

C. Tetra-, Penta-, and Hexatomic Alcohols.

These alcohols can react respectively with four, five, or six molecules of a monobasic acid to form neutral ethers, and consequently four, five, or six alcoholic hydroxyls are to be assumed as present in their molecules.

The atomicity of an alcohol is determined by the number of acetyl groups which are found to be present in the ether which results upon heating it with acetic anhydride and acetate of soda, thus:

$$C_6H_8(OH)_6 + 6(C_2H_3O)_2O = C_6H_8(O.C_2H_3O)_6 + 6C_2H_4O_2.$$

The ether of any alcohol in question may also be prepared by the aid of an acid containing halogen, bromo-benzoic acid being especially suitable for this; and from the amount of bromine found in the ether, the number of acid radicles which have entered the molecule, *i.e.* the number of replaced hydroxyls, can be deduced.

The higher atomic alcohols are solid crystalline compounds of sweet taste. They are in part natural products, and they also result from the reduction of the corresponding monobasic oxy-acids (mannonic acid, etc.) by sodium amalgam. (*E. Fischer*, B. 22, 2204.) Conversely, cautious oxidation by bromine

water transforms them first into those sugars, and then into the acids. As a rule they cannot be volatilized without decomposition. Their derivatives are exactly analogous to those of glycol and glycerine.

Their *constitution* follows from the law already repeatedly referred to at pp. 142, 203, etc., viz., that not more than one hydroxyl group can be bound to one carbon atom without the immediate separation of water, so that a tetratomic alcohol must contain at least four, and a hexatomic alcohol at least six atoms of carbon. The tetratomic alcohol erythrite, $C_4H_{10}O_4$, = $C_4H_6(OH)_4$, has thus the formula:

$$CH_2(OH)—CH(OH)—CH(OH)—CH_2(OH);$$

and mannite, the lowest of the hexatomic alcohols, $C_6H_{14}O_6$, = $C_6H_8(OH)_6$, the formula:

$$CH_2(OH)—CH(OH)—CH(OH)—CH(OH)—CH(OH)—CH_2(OH).$$

These alcohols, which are the lowest theoretically possible, *i.e.* which contain the smallest possible number of carbon atoms in the molecule, are at the same time the only ones of special importance.

1. **Tetratomic alcohols. Ortho-carbonic ether**, *Bassett's* carbonic ether, $C(OC_2H_5)_4$, is to be regarded as the ether of the hypothetical alcohol, $C(OH)_4$, which may be looked upon as the hydrate of carbonic acid, but is itself incapable of existence. It is a liquid of ethereal odour, boiling at 159°.

Erythrite or *phycite* (*Butane-tetrol*), $C_4H_6(OH)_4$ (*Stenhouse*), occurs in the free state in Protococcus vulgaris, and combined with orsellinic acid as ether (erythrin), in many lichens and algæ. Large quadratic crystals, difficultly soluble in alcohol and insoluble in ether. M. Pt. 112°, B. Pt. about 300°. Yields secondary butyl iodide when heated with hydriodic acid (pp. 93 and 72, 3 b). **Penta-erythrite**, probably $C(CH_2OH)_4$, has been prepared synthetically (A. 265, 316).

2. **Pentatomic alcohols. Pentoxy-pentane**, *Arabite*, $C_5H_7(OH)_5$, (from arabinose by reduction). **Xylite**, which results in a similar manner from xylose, is isomeric with it; and Rhamnite, $C_5H_6(OH)_5CH_3$, M. Pt. 121°, from rhamnose, is homologous.

3. **Hexatomic Alcohols. Mannite**, $C_6H_{14}O_6$, = $C_6H_8(OH)_6$ (*Proust*, 1800), is found in many plants, for instance, in the larch, in Viburnum Opulus, in celery, in the leaves of Syringa vulgaris, in sugar cane, in Agaricus integer (of the dry substance of which it forms 20%), in rye bread, and especially in the manna ash, Fraxinus ornus, the dried juice of which constitutes manna. It can be prepared from grape sugar, or, still better, from fruit sugar, from which it only differs in composition

by containing two atoms of hydrogen more in the molecule, by reduction with sodium amalgam:

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6.$$

Fine needles or rhombic prisms, easily soluble in cold water and boiling alcohol. Dextro-rotatory. A lævo-rotatory and an inactive modification are also known (see Mannonic acid). M. Pt. 166°. When heated it is converted into its anhydrides, **Mannitan**, $C_6H_{12}O_5$, and **Mannide**, $C_6H_{10}O_4$. Cautious oxidation converts mannite first into lævulose (B. 19, 911), mannose (p. 315) being formed at the same time. Nitric acid oxidizes it to saccharic acid; hydriodic reduces it to secondary hexyl iodide (p. 75).

Nitro-mannite, $C_6H_8(O.NO_2)_6$, forms glancing needles and is explosive. The **Acetate**, $C_6H_8(O.C_2H_3O)_6$, is prepared from acetic anhydride.

Dulcite, *melampyrine*, $C_6H_8(OH)_6$, stereo-isomeric with mannite, is, like the latter, widely distributed in nature, being found *e.g.* in the varieties of melampyrum and evonymus, in the dulcite manna of Madagascar, etc. Results from the reduction of milk sugar and galactose by sodium amalgam. Nitric acid oxidizes it to mucic acid, and hydriodic acid reduces it to the same hexyl iodide as in the case of mannite. *Dulcite is optically inactive*, in consequence of the symmetrical structure of its molecule (as in the case of inactive tartaric acid). See B. **24**, 528; **25**, 1248, 2564.

Sorbite, $C_6H_{14}O_6 + \frac{1}{2}H_2O$, is stereo-isomeric with mannite. It is present in service berries, and is formed by the reduction of *d*-glucose and of *d*-levulose; *it becomes slightly dextro-rotatory after the addition of borax. Rhamno-hexite*, $C_6H_7(OH)_6CH_3$ (*cf.* B. **23**, 3102).

The carbohydrates are closely related to the penta- and hexatomic alcohols. The latter differ from the former in not being fermentable by yeast, and in not reducing an alkaline cupric solution, dulcite excepted.

Perseite, *manno-heptite*, $C_7H_{16}O_7$, is a heptatomic alcohol, obtainable from the seeds of *Laurus Persea*. It has been synthetized by *E. Fischer* (B. **23**, 930).

Gluco-heptite, $C_7H_{16}O_7$. **Manno-octite**, $C_8H_{18}O_8$, *an octatomic alcohol* (B. **23**, 2226). **Gluco-octite**, $C_8H_{18}O_8$. **Gluco-nonite**, $C_9H_{20}O_9$.

Oxidation Products of the Polyatomic Alcohols.

Just as the monatomic alcohols are oxidized to aldehydes, ketones and acids, so the polyatomic alcohols pass, on oxidation, into polyatomic aldehydes and ketones, and polybasic acids.

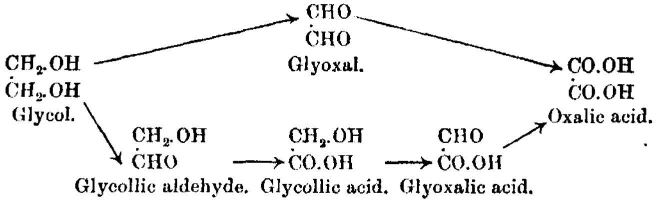
Further, by this oxidation of the polyatomic alcohols there result, or may result, not only aldehydes, ketones and acids, but also numerous compounds which possess a double chemical nature in so far as they unite in themselves the characteristics of more than one of these classes of compounds. These are the aldehyde-

alcohols, which are at the same time aldehyde and alcohol, the ketone-alcohols, at the same time ketone and alcohol, the alcohol-acids, aldehyde-acids, ketone-acids and ketone-aldehydes.

An aldehyde-acid, for instance, is capable, as an acid, of forming salts, ethers and amides on the one hand, compounds which possess all the characteristic properties of the ethers, etc.; and on the other, as an aldehyde, it is able to reduce an ammoniacal silver solution, to combine with $NaHSO_3$, and to react with hydroxylamine, etc.

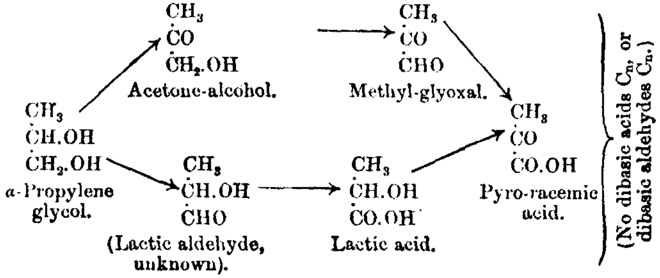
Summary of the Oxidation Products.

(*a*) Of the diatomic di-primary alcohols.



Possible products: diatomic aldehydes, dibasic acids, alcohol-aldehydes, alcohol-acids, aldehyde-acids.

(*b*) Of the diatomic primary-secondary alcohols.



Possible products: aldehyde-alcohols, ketone-alcohols, ketone-aldehydes, alcohol-acids, ketone-acids.

(*c*) Of the diatomic di-secondary alcohols: ketone-alcohols, di-ketones. (No dibasic acids or alcohol-acids, C_n.) *e.g.*:—

CH_3—CH.OH		CH_3—CH.OH		CH_3—CO
|	⟶	|	⟶	|
CH_3—CH.OH		CH_3—CO		CH_3—CO
Di-secondary butylene glycol.		Dimethyl-ketol.		Di-acetyl.

(*d*) Of the other diatomic alcohols: easy to tabulate.

(*e*) The tri- and polybasic alcohols are capable of yielding the most various products upon oxidation, especially polyatomic ketone-alcohols, alcohol-acids, ketone-acids, and polybasic acids.

We have now, therefore, to consider the aldehyde-alcohols, ketone-alcohols, polyatomic aldehydes and ketones, monobasic alcohol-acids, aldehyde-acids and ketonic acids, and polybasic acids.

The most important among these compounds are the alcohol-acids, the polybasic acids, and the ketonic acids. For the sake of convenience the polyatomic monobasic acids will be treated of first.

IX. POLYATOMIC MONOBASIC ACIDS AND COMPOUNDS RELATED TO THEM.

A. Diatomic Monobasic Acids.

Summary.

Glycollic acid, $CH_2(OH)(CO_2H)$	Oxy-valeric acids, $C_4H_8(OH)(CO_2H)$
Oxy-propionic acids, $C_2H_4(OH)(CO_2H)$	Oxy-caproic acids, $C_5H_{10}(OH)(CO_2H)$
Oxy-butyric acids, $C_3H_6(OH)(CO_2H)$	etc.

The diatomic alcohol-acids or diatomic monobasic acids are compounds which unite in themselves the characteristics of an alcohol and of an acid, and are consequently capable of forming derivatives as alcohols, as acids, and as both together.

These derivatives are in part easily saponifiable, and correspond therefore with the acid derivatives, *i.e.* the compound ethers, chlorides and amides; in part they are relatively stable as regards saponifying agents, and therefore correspond with the alcoholic derivatives, *i.e.* the ethers, amine bases, etc., (see table, p. 226).

The lowest members of the series of diatomic monobasic acids, *which are at the same time the most important*, are glycollic acid and lactic acid, both syrupy liquids which solidify to crystalline masses in the exsiccator, and easily give up water to form anhydride.

They cannot be volatilized without decomposition. They are readily soluble in water, and for the most part also in alcohol and ether.

They are termed diatomic, because they may result from the oxidation of the diatomic alcohols, and contain in accordance with theory two hydroxyls. As acids they are monobasic. They are also frequently called oxy-fatty acids, on account of their being derived from the fatty acids by the exchange of one hydrogen atom for hydroxyl, in the same way as the alcohols are derived from the hydrocarbons:

$CH_3—CO_2H$, *acetic acid*; $CH_2(OH)—CO_2H$, *oxy-acetic acid.*

We may also regard them as carboxylic acids of the monatomic alcohols, *e.g.* lactic acid, $C_2H_4(OH).CO_2H$, is ethyl alcohol-carboxylic acid.

Formation. 1. By the regulated oxidation of the glycols, (see Summary, p. 220).

2. From the fatty acids, through their mono-haloid substitution products, the halogen of these being easily replaced by hydroxyl, either by means of moist oxide of silver or often by prolonged boiling with water alone:

$$CH_2Cl.CO_2H + H_2O = CH_2(OH).CO_2H + HCl.$$

This reaction is conditioned by the halogen having the α-position with respect to the hydroxyl (cf. p. 184).

For a reaction of these haloid-substitution products in a different direction, see β- and γ-oxyacids.

3. From the aldehydes and ketones containing one atom of carbon less, by the preparation of their hydrocyanic acid compounds, (see pp. 144 and 155), and saponification of the latter. Thus, from aldehyde is produced ethylidene cyanhydrin, and from this lactic acid:

$$CH_3.CH(OH)(CN) + 2H_2O = CH_3.CH(OH).CO_2H + NH_3.$$

Since the aldehydes and ketones are easily got from the corresponding alcohols, this reaction furnishes a means of preparing the acids, $C_nH_{2n}(OH)(CO_2H)$, from the alcohols, $C_nH_{2n+1}(OH)$, *i.e.*, of introducing carboxyl into the latter in place of hydrogen; this is a very important synthesis.

4. From the glycollic cyanhydrins by saponification, *e.g.* ethylene lactic acid from ethylene cyanhydrin:

$$CH_2(OH)—CH_2.CN + 2H_2O = CH_2(OH)—CH_2—CO_2H + NH_3.$$

The cyanhydrins being easily obtained from the glycols, this formation of oxy-acids represents an exchange of a hydroxyl of the glycol for carboxyl, and is analogous to the formation of acetic acid from methyl alcohol.

5. By the reduction of aldehyde-acids or ketonic acids, *e.g.* lactic from pyroracemic acid (p. 229). This reaction corresponds with the formation of the alcohols from the aldehydes or ketones by reduction.

6. By the action of nitrous acid (N_2O_3) upon amido-acids (see Glycocoll); *a reaction analogous to the formation of alcohols from amines.*

7. Oxy-acids of the fatty series containing an equal number of carbon atoms result by *direct oxidation*, if a CH-group, *i.e.* a "tertiary" hydrogen atom, is present in the original acid:

$$(CH_3)_2{=}CH—CO_2H + O = (CH_3)_2{=}C(OH)—CO_2H$$

Isobutyric acid. α-Oxy-isobutyric acid.

Constitution and *Isomers.* As oxy-compounds of the fatty acids, the acids of the foregoing series can exist in as many modifications as there are possible mono-haloid substitution products of the fatty acids. Thus there is only one glycollic acid, corresponding to mono-chloracetic acid, but two lactic acids—corresponding to α- and β-chloro-propionic acids—are possible, and both actually exist; they are designated as α- and β-oxy-propionic acids:

$CH_3—CHCl—CO_2H$ α-Chloro-propionic acid.	$CH_3—CH(OH)—CO_2H$ α-Oxy-propionic acid or common lactic acid.
$CH_2I—CH_2—CO_2H$ β-Iodo-propionic acid.	$CH_2(OH)—CH_2—CO_2H$ β-Oxy-propionic acid or ethylene lactic acid.

From the two butyric acids can be theoretically derived:

(*a*) From the normal acid:

$$\underset{\gamma}{CH_3}—\underset{\beta}{CH_2}—\underset{\alpha}{CH_2}—CO_2H,$$

an α-, β-, and γ-oxy-butyric acid;

(*b*) From iso-butyric acid :

$$\begin{matrix}\beta\ CH_3 \\ \beta\ CH_3\end{matrix}\!\!>\underset{\alpha}{CH}-CO_2H,$$

an α- and β-oxy-isobutyric acid.

The constitution of these oxy-acids is often apparent from their formation alone. Thus the preparation of common lactic acid from aldehyde, CH_3—CHO, according to method 3, shows that it contains the group CH_3—CH=, "ethylidene"; it is therefore termed "ethylidene lactic acid." On the other hand the formation of β-oxy-propionic acid from glycol, *i.e.* glycol cyanhydrin, according to 4, is a proof of its containing the group —CH_2—CH_2—, "ethylene"; hence the name "ethylene lactic acid."

The behaviour of the oxy-acids usually explains their constitution also; if they can be oxidized, for instance, to dibasic acids (which contain two carboxyls), then they must contain a primary alcohol group, —CH_2.OH, since only such a group yields a new carboxyl on oxidation. Ethylene lactic acid is therefore a "primary" alcohol-acid. Its isomer, ethylidene lactic acid, is similarly a "secondary" alcohol-acid, while α-oxy-isobutyric acid is a "tertiary" alcohol-acid, *i.e.* acid and tertiary alcohol at the same time.

Behaviour. 1. The double chemical character of the oxy-acids will be gone into more particularly under glycollic acid. As acids they form salts, compound ethers and amides; as alcohols they yield ethers, amines, etc. Among those derivatives the alcoholic amines of the acids, the so-called amido-acids, are of especial interest. (See Glycocoll, p. 227).

2. The oxy-acids form different kinds of anhydrides, viz.:—(*a*) as alcohols, (see di-glycollic acid); (*b*) one molecule as alcohol forms with a second molecule as acid, a compound ether, with separation of H_2O, (see glycollic anhydride); (*c*) such a formation of ether as this proceeds a second time, (see glycolide); (*d*) one molecule loses H_2O, with formation of an "intra-molecular" anhydride, a so-called *lactone*, (see p. 233).

3. For behaviour upon oxidation, see p. 220, and also the individual compounds.

4. Just as the alcohols go into olefines with separation of water, so

can many of the oxy-acids, especially the β-, be transformed into unsaturated monobasic acids. (See hydracrylic acid, p. 232).

5. Halogens oxidize and do not substitute.

6. Warming with HI gives rise to the corresponding fatty acids, just as the alcohols are converted by this reagent into hydrocarbons.

7. When the α-oxy-acids are warmed with dilute sulphuric acid, formic acid is separated and the aldehyde or ketone which would give rise to the acid, according to method 3, is reproduced. The β-oxy-acids on the other hand break up in this way, and also when heated alone, into water and acids of the acrylic series. The α-, β-, γ-, etc. oxy-acids also differ from each other in the facility with which they form anhydrides. (See Lactones.)

Glycollic acid (*Ethanolic acid*), $CH_2(OH)—CO.OH$ (*Strecker*, 1848).

Occurrence. In unripe grapes, in leaves of the wild vine, etc.

Formation. (See also p. 222.) 1. By the oxidation of glycol with dilute HNO_3 (*Wurtz*).

2. Together with glyoxal and glyoxalic acid, by the oxidation of alcohol with dilute HNO_3. Further, by the oxidation of glucoses by Ag_2O (A. **205**, 193).

3. By the reduction of oxalic acid with $Zn + H_2SO_4$.

4. From formic aldehyde synthetically, according to method 3, p. 222.

5. Preparation from mono-chloracetic acid, according to p. 222; best when boiled with marble (A. **200**, 76).

Properties. Colourless needles or plates, stable in the air, and easily soluble in water, alcohol, and ether. M. Pt., 80°. Nitric acid oxidizes it to oxalic acid. The alkaline salts are hygroscopic, the calcium salt and the magnificent blue copper salt sparingly soluble in water.

Derivatives. (See table, p. 226.) As an acid, glycollic acid forms salts, compound ethers,—*e.g.* glycollic ethyl ether,—a chloride, glycollyl chloride, and glycollamide, all of which are readily saponified, some of them even on warming with water. All those derivatives still retain their alcoholic character. If, on the other hand, glycollic acid forms derivatives as an alcohol, the properties of the alcoholic derivatives in question are combined with those of an acid, since the hydroxyl of the

alcoholic group, —CH_2OH, enters into reaction, while the carboxyl group remains unchanged. These derivatives are either ethers, such as ethyl-glycollic acid (see table), or *e.g.* amines, such as glycocoll, and, as alcoholic derivatives, they are not saponifiable; or they are compound ethers of glycollic acid as alcohol, *e.g.* acetyl-glycollic acid, $CH_2(O.C_2H_3O)—CO_2H$, or mono-chloracetic acid, $CH_2.Cl—CO_2H$ (the hydrochloric ether of glycollic acid), and then they are of course saponifiable. These latter compounds still retain their acid character and therefore form, on their part, compound ethers, chlorides and amides, which are readily broken up backwards by saponification. The following table gives a summary of the more important derivatives of glycollic acid.

Acid Derivatives.	*Alcoholic Derivatives.*	*Mixed Derivatives.*
$CH_2(OH)—CO.ONa$ Sodium glycollate.		$CH_2(ONa)—CO.ONa$ Di-sodium glycollate. Hygroscopic; decomp. by H_2O into Na salt and NaOH.
$CH_2(OH)—CO.OC_2H_5$ Ethyl glycollate. Liquid, B. Pt. 160°.	$CH_2(OC_2H_5)—CO.OH$ Ethyl-glycollic acid. Liquid, B. Pt. 206°.	$CH_2(OC_2H_5)—CO(OC_2H_5)$ Ethylic ethyl-glycollate. Liquid, B. Pt. 152°.
$CH_2(OH)—CO.Cl$ Glycollyl chloride. Oil; decomposes on volatilizing.	$CH_2Cl—CO.OH$ Mono-chloracetic acid.	$CH_2Cl—COCl$ Mono-chlor-acetyl chloride. Liquid, B. Pt. 120°, of suffocating odour.
$CH_2(OH)—CO.NH_2$ Glycollamide. Crys. M. Pt. 120°; does not form salts with bases.	$CH_2(NH_2)—CO.OH$ Glycocoll. Crys. M. Pt. 236°. Forms salts with acids and bases.	$CH_2(NH_2)—CO(NH_2)$ Glycocollamide. Crys.

To the compounds of the second vertical row belong also, among others, **Thio-glycollic acid** (1-*Ethane-thiol*-2-*Acid*), $CH_2(SH)—CO.OH$, which is at the same time an acid and a mercaptan; to those of the third row belong mixed compounds such as $CH_2(NH_2)—CO(OC_2H_5)$ (see Glycocoll). It is easy to see that the corresponding derivatives of the first and second vertical rows are always isomeric.

Anhydrides of Glycollic acid. 1. **Di-glycollic acid,** $C_4H_6O_5 = O(CH_2—CO.OH)_2$, is an alcoholic anhydride and a dibasic acid. It is obtained *e.g.* by boiling mono-chloracetic acid with lime. Large rhombic prisms. Being an alcoholic ether, it is not saponified on boiling with alkalies, but on heating with concentrated hydrochloric acid to 120°. As a dibasic acid it yields:

2. **Di-glycollic anhydride,** $C_4H_4O_4 = O(CH_2—CO)_2O$.

3. **Glycollic anhydride,** $C_4H_6O_5 = CH_2(OH)—CO.O(CH_2—CO.OH)$, is a compound ether-anhydride, which is formed upon heating glycollic acid to 100°. It becomes hydrated again when boiled with water.

4. **Glycolide,** $C_4H_4O_4 = \begin{array}{l} CH_2—O—CO \\ | \qquad\qquad | \\ CO—O—CH_2 \end{array}$, is an ether-acid anhydride isomeric with 2 (and with fumaric acid), which results upon distilling bromoacetate of sodium in a vacuum. Lustrous plates; M. Pt. 87°. It becomes hydrated again upon boiling with water.

Glycocoll (*Amino-ethanoic acid*), *glycocine*, *amido-acetic acid*, $CH_2(NH_2)—CO.OH$ (*Braconnot*, 1820). This is the simplest representative of the important class of "amino-(or amido-) acids," so called because they are derived from the fatty acids by the exchange of a hydrogen atom of the hydrocarbon radicle for amidogen, *e.g.* $CH_3.CO_2H$, acetic acid; $CH_2(NH_2).CO_2H$, amido-acetic acid. Its methods of formation include those of the other amido-acids.

Formation. 1. By the action of concentrated ammonia upon monochlor-acetic acid (*Heintz*, A. **122**, 261; *Kraut*, A. **266**, 292):

$$CH_2Cl—CO_2H + 2NH_3 = CH_2(NH_2)—CO_2H + NH_4Cl$$

(cf. also B. **23**, Ref. 654). Di- and Tri-glycollamic acids, $NH(CH_2—CO_2H)_2$ and $N(CH_2—CO_2H)_3$, are produced at the same time.

α-Chloropropionic acid in like manner yields alanine with ammonia (see Lactic acid), and so on.

2. By boiling glue with alkalies or acids.

3. Together with benzoic acid by decomposing hippuric acid, *i.e.* benzoyl-glycocoll, by HCl:

$$\underbrace{CH_2[NH(COC_6H_5)]—CO_2H}_{\text{Hippuric acid.}} + H_2O = CH_2(NH_2)CO_2H + \underbrace{C_6H_5CO.OH.}_{\text{Benzoic acid.}}$$

4. Together with cholic acid, by the analogous decomposition of glycocholic acid, $C_{26}H_{43}NO_6$.

5. From cyano-carbonic ether, $CN—CO.OC_2H_5$, and nascent hydrogen, or from cyanogen and hydriodic acid:

$$CN—CN + 2H_2 + 2H_2O = CH_2(NH_2)—CO.OH + NH_3.$$

6. By the reduction of isonitroso-fatty acids (p. 185).

7. (Of the homologues of glycocoll): By treating ethylidene-cyanhydrin (p. 144), etc. with alcoholic ammonia, or aldehyde-ammonias with hydrocyanic acid, amido-cyanides are formed, *e.g.* $CH_3—CH(NH_2)(CN)$, which are saponified to amido-acids upon boiling with HCl.

Properties. Glycocoll forms large colourless rhombic prisms, easily soluble in water, but insoluble in absolute alcohol and ether. It has a sweet taste, hence the name "gelatine sugar" or glycocoll (γλυκύς, sweet, κόλλα, glue). It melts at 236°, with much decomposition.

Behaviour. Glycocoll, like all the amido-acids, unites in itself the properties of a base (being, as an alcoholic amine, non-saponifiable) and those of an acid. It therefore forms salts with acids as well as with bases, *e.g.* glycocoll hydrochlorate, $C_2H_5NO_2.HCl$, which crystallizes in prisms, and the characteristic copper salt, glycocoll copper, $(C_2H_4NO_2)_2Cu + H_2O$, which crystallizes in blue needles, the latter being obtained by dissolving copper oxide in a solution of glycocoll. Most of the other amido-acids also form characteristic copper salts of this nature, which serve for their separation. Glycocoll also yields compounds with salts, and, as an acid, forms an ethyl ether, an amide, etc. (see table, p. 226). Heated with BaO, it is decomposed into methylamine and CO_2, while N_2O_3 converts it into glycollic acid (the normal reaction of the primary amines). Ferric chloride produces with it an intense red, and copper salts a deep blue colouration.

Glycocol ethyl ether yields with N_2O_3 the interesting **Diazo-acetic ether**, $CN_2H—CO.OC_2H_5$, from which, by a complicated reaction, hydrazine, $NH_2—NH_2$, and its hydrate were first prepared; and, from the latter, the remarkable compound, Hydrazoic acid, N_3H (*Curtius* J. pr. Ch. (2) **38**, 396, 472; **43**, 207; B. **24**, 3341). See also under Amido-guanidine.

Constitution (see B. **16**, 2650). Free glycocoll may be regarded as an intramolecular salt, corresponding to the formula $CH_2\langle{}^{NH_3}_{CO.O}\rangle$ (see Betaine).

Alkyl derivatives of Glycocoll:

Methyl-glycocoll or Sarcosine,	Tri-methyl-glycocoll or Betaïne,	Acetyl-glycocoll or Aceturic acid,
$CH_2—NH(CH_3)$ $\dot{C}O.OH$	$CH_2—N(CH_3)_3\rangle$ $\dot{C}O.O$	$CH_2—NH(C_2H_3O)$ $\dot{C}O.OH.$
(a decomposition product of creatine and caffeine).	(contained in beetroot and related to choline).	etc.

The above have all been prepared synthetically.

Lactic acids, $C_3H_6O_3$, = $C_2H_4(OH)(CO_2H)$. (*Wislicenus,* A. 128, 1; 166, 3; 167, 302, 346.) As has been already mentioned at p. 223, two isomeric lactic acids are theoretically possible, viz., α- and β-oxy-propionic acids, or ethylidene- and ethylene-lactic acids, and both of these are known.

The minute investigation of the different lactic acids has been of very great importance for the development of chemical theory; they were formerly held to be dibasic, and the recognition of their diatomic monobasic nature has materially contributed to the acceptation of the theory of the linking of atoms.

According to the theory of *Le Bel* and *van 't Hoff* (p. 40), two stereoisomeric modifications of ethylidene-lactic acid are possible, seeing that it contains an asymmetric carbon atom, viz. a laevo- (*l*-) and a dextro- (*d*-) rotatory form; and, by mixing these together, a third optically inactive (*i*-) acid is produced. The two last have long been known, but the laevo-acid has only been discovered recently, the theory thereby receiving further confirmation.

Modes of Formation.	Fermentation lactic acid	Ethylene-lactic acid.
1. By the regulated oxidation of	α-Propylene glycol, CH_3-CH(OH)-CH_2(OH).	β-Propylene glycol, CH_2(OH)-CH_2-CH_2(OH)
2. By the exchange of halogen for hydroxyl from	α-Chloro-propionic acid, CH_3—CHCl—CO.OH.	β-Iodo-propionic acid, CH_2I—CH_2—CO.OH.
3. By saponification of	Aldehyde-cyanhydrin, CH_3—CH(OH)—CN.	Ethylene-cyanhydrin, CH_2(OH)—CH_2—CN.
4. By action of N_2O_3 upon	Alanine, CH_3-CH(NH_2)-CO.OH.	
5. By the reduction of	Pyro-racemic acid, CH_3—CO—CO.OH.	
6. By the lactic fermentation of sugar, etc.		

1. i-Ethylidene-lactic acid (*2-Propanolic acid*), *ordinary fermentation lactic acid,* CH_3—CH.(OH)—CO_2H. Discovered by *Scheele,* and recognized as oxy-propionic acid by *Kolbe.* Occurs in opium, sauerkraut, and in the gastric juice.

Preparation. This depends upon the so-called lactic fermentation of sugars, *e.g.* milk, cane and grape sugars, and of substances related to them, such as gum and starch; it is induced by the *lactic bacillus* [which forms small rods (*Küppe*)]. The fermentation proceeds best at a temperature of 34°–35°, in a nearly neutral solution, this last condition being attained by the addition of chalk or zinc white to the fermenting mixture. The free acid can then be liberated from the lactate of zinc by sulphuretted hydrogen. When a non-homogeneous ferment (*e.g.* cheese) is used, the lactic acid at first produced is transformed by other organisms into butyric acid (p. 174).

Lactic acid is also produced in large quantity by heating grape or cane sugar with caustic potash solution of a certain degree of concentration (B. 15, 136). The relations of lactic acid to the sugar varieties appear at a superficial glance to be very simple; thus grape sugar, $C_6H_{12}O_6$, and lactic acid, $C_3H_6O_3$, are polymers.

Lastly, the inactive acid is produced by mixing equal quantities of the two active modifications. In syntheses the latter are formed in equal amounts, and hence the inactive acid is obtained.

Properties. The acid has not been obtained free from water. When its solution is evaporated in an exsiccator, a thick, non-crystallizing and hygroscopic syrup is got, which is miscible with water, alcohol and ether, and which gradually gives up water, with the formation of (solid) lactic anhydride, $C_6H_{10}O_5$, before all the water of solution has been got rid of. When heated, it partly goes into the anhydride, lactide, $C_6H_8O_4$, and partly breaks up into aldehyde, CO, and H_2O. Similarly it decomposes into aldehyde and formic acid upon heating with dilute sulphuric acid to 130°, concentrated sulphuric giving rise to carbon monoxide instead of formic acid:

$$CH_3—CH(OH)—CO_2H = CH_3—CHO + HCO_2H.$$

Upon oxidation it yields acetic and carbonic acids; hydrobromic acid converts it into α-bromo-propionic acid, and boiling with hydriodic acid into propionic acid itself.

The inactive acid is split up into the two active modifications by the crystallization of the strychnine salts; further, when the fungus *penicillium*

glaucum is sown in a solution of the inactive acid, the laevo- acid is assimilated more rapidly than the dextro-, and the solution thus becomes dextrorotatory (cf. p. 39).

Calcium lactate, $(C_3H_5O_3)_2Ca + 5H_2O$: warty masses of microscopic rhombic needles. **Zinc lactate**, $(C_3H_5O_3)_2Zn + 3H_2O$: *glancing needles.* **Ferrous lactate**, $(C_3H_5O_3)_2 + 3H_2O$: bright yellow needles; both the ferrous and zinc salts are used in medicine. When sodium lactate is heated with sodium, **Di-sodium lactate**, $CH_3—CH(ONa)—CO_2Na$, which is at the same time a salt and an alcoholate, is formed.

The *Derivatives* of lactic acid are derivatives of it either as acid or as alcohol, and are perfectly analogous to those of glycollic acid (see table, p. 226). Thus **Ethyl-lactic acid**, $CH_3—CH(OC_2H_5)—CO_2H$, a thick acid liquid which boils almost without decomposition,* corresponds to ethyl-glycollic acid; **Ethyl lactate**, which can be distilled without decomposition, to ethyl glycollate; **Lactamide**, $CH_3—CH(OH)—CO.NH_2$ to glycollamide, and **Alanine**, $CH_3—CH(NH_2)—CO.OH$, to glycocoll. Alanine results from the action of hydrocyanic acid upon aldehyde-ammonia (see p. 228), and forms hard needles of a sweetish taste.

By the action of PCl_5, lactyl chloride, $CH_3—CHCl—CO.Cl$ (p. 192) is formed; as the chloride of α-chloro-propionic acid it yields the latter acid and HCl with water. The acid just named is therefore to be regarded as the hydrochloric ether of lactic acid.

The following anhydrides of lactic acid are known:

1. **Lactylic acid** or **Lactic anhydride**, $C_6H_{10}O_5$, which is analogous to *glycollic anhydride, and forms a yellow amorphous mass*; 2. **Lactide**, $C_6H_8O_4$, analogous to glycolide (tables, M.-Pt. 125°); 3. **Di-lactic acid**, $C_6H_{10}O_5$, the alcoholic anhydride, analogous to di-glycollic acid.

2. **d-Ethylidene-lactic-acid**, *Sarco-lactic acid, para-lactic acid*, $CH_3—CH(OH)—CO_2H$ (*Liebig*). This occurs in the juice of flesh, and is therefore to be found in Liebig's extract of meat. It results from certain fermentations. In its chemical properties it is almost identical with ordinary lactic acid; for instance, it possesses an equal facility in forming lactide or

* By the entrance of the ethylic group, the hydroxyl is in a certain degree paralysed as regards its action, in consequence of which ethyl-lactic acid resembles propionic acid much more nearly than lactic acid itself does.

aldehyde. Its salts differ to some extent, however, from those of the latter; thus, the zinc salt: $+2H_2O$, is much more easily soluble, and the calcium salt: $+4H_2O$, much more difficultly soluble than the corresponding common lactates.

3. **l-Ethylidene-lactic acid** is obtained from the fermentation of cane sugar by means of the *l-lactic bacillus* (Monatsh. f. Chem. 11, 551).

4. **Ethylene-lactic acid** (*3-Propanolic acid*), *hydracrylic acid*, $CH_2(OH)—CH_2—CO.OH$ (*Wislicenus*, A. 128, 1), forms a syrupy mass. It differs from lactic acid: (*a*) By its behaviour upon oxidation, yielding carbonic and oxalic acids, and not acetic; (*b*) By not yielding an anhydride when heated, but by breaking up into water and acrylic acid, hence the name hydracrylic acid:

$$CH_2(OH)—CH_2—COOH = CH_2{=}CH—COOH + H_2O;$$

(*c*) In solubility, and in the amount of water of crystallization of its salts (*e.g.* zinc salt: $+4H_2O$, very easily soluble in water; calcium salt: $+2H_2O$).

Oxy-butyric acids, (see p. 223).

β-Oxy-butyric acid, $CH_3—CH(OH)—CH_2—CO_2H$, a syrup, is related to aldol and aceto-acetic acid. An optically active (—) modification is contained in diabetic urine and blood.

γ-Oxy-butyric acid, $CH_2(OH)—CH_2—CH_2—CO_2H$, is only capable of existence in its salts and not in the free state, as it breaks up into water and its lactone, butyro-lactone.

α-Oxy-isobutyric acid, $(CH_3)_2{=}C(OH)—CO_2H$, (*Wurtz*), results from acetone cyanhydrin (p. 155), and is therefore also called acetonic acid.

Amido-butyric acids are known, *e.g.* **Piperic acid**, $C_3H_6(NH_2)(CO_2H)$.

Oxy-valeric acids. Several **amido-valeric acids** have been prepared synthetically, while others have been obtained by the decomposition of albumen and of conine and piperidine derivatives, and have also been found in the pancreas of the ox.

Oxy-caproic acids. Leucine or **α-Amido-caproic acid**, $CH_3—CH_2—CH_2—CH_2—CH(NH_2)—CO_2H$, is a derivative of α-oxy-caproic or leucic acid (*Strecker*); it forms fatty glancing plates and, like other amido-acids, is nearly related to albumen. It is found in old cheese, also abundantly in the animal organism in the gastric salivary gland, and in the shoots of the vetch and gourd, etc. It forms, along with tyrosine, a con-

stant product of the digestion of albumen in the small intestine and of the decay of albuminous substances, and results from the latter by boiling them with alkalies or acids. It also appears to have been prepared synthetically. It closely resembles glycocoll, and forms a characteristic sparingly soluble blue copper salt. Leucine is dextro-rotatory. A lævo- and an inactive modification are also known (B. 24, 669).

Conic acid, $C_7H_{15}NO_2$, and **Homo-conic acid**, $C_8H_{17}NO_2$, are higher homologues of leucine which have been prepared from conine.

Oxy-stearic acid, $C_{18}H_{36}O_3$, is obtained by the action of cold concentrated H_2SO_4 on oleic acid—(addition of H_2O)—and forms a white mass. Its sulphuric ether or **Oxy-stearo-sulphuric acid**, $C_{18}H_{35}O_2(OSO_3H)$, is of importance for the manufacture of Turkey red.

Coccerylic acid, $C_{31}H_{62}O_3$, occurs in cochineal wax, combined with cocceryl alcohol.

The two following are diatomic monobasic acids: **Ricinoleic acid**, $C_{18}H_{34}O_3$, from castor-oil (its glycerine ester); the so-called *Ricinoleic-sulphonic acid*, obtained by acting on castor-oil with sulphuric acid, is largely used in the Turkey-red industry. **Rapinic acid**, $C_{18}H_{34}O_3$ (from rape-seed oil), is isomeric with the above.

If the hydroxyl of the acids of this group is linked directly to one of the unsaturated carbon atoms, compounds are formed which possess materially different properties (see Oxy-acrylic acid, p. 240).

Appendix. Lactones.*

The γ-oxy-acids (see γ-oxy-butyric acid) are very unstable in the free state, so that when an acid is added to their salts, not the oxy-acids themselves but anhydrides are obtained, *e.g.* butyro-lactone (see pp. 224, 225):

$$\underset{\gamma\text{-Oxy-butyric acid.}}{CH_2(OH)—CH_2—CH_2—CO.OH} = \underset{\text{Butyro-lactone.}}{\underbrace{CH_2—CH_2—CH_2—CO}_{O}} + H_2O.$$

These lactones are to be regarded as intramolecular anhydrides (*i.e.* 1 mol. acid − 1 mol. H_2O), or ethers, the acid part of the molecule etherifying in some degree the alcoholic part.

The lactones of the γ-oxy-acids, "γ-lactones," are for the most part neutral liquids of faint aromatic odour, easily soluble in alcohol and ether, and distilling without decomposition. They dissolve in alkalies to the salts of the corresponding oxy-acids, and form brominated fatty acids with HBr, and amido-acids or amides of γ-oxy-acids with NH_3 (B. 23, Ref. 234).

δ- and β-, but only a few α-lactones, from δ-, β-, and α-oxy-acids, are also known. They show marked differences in the ease with which they are

* "O.N." Olides.

formed and in their stability, the γ-lactones being the most stable. For α-Lactones, see B. 24, 4070.

The formation of lactones by warming the unsaturated acids, $C_nH_{2n-2}O_2$, which are isomeric with them, with HBr or with moderately concentrated H_2SO_4, is worthy of note.

For details, see *Fittig* and his pupils, A. **208**, 37, 111; **216**, 26; **255**, 1, 275; **256**, 50; **268**, 110. For the production of *Oxetones* from lactones, see A. **267**, 186.

B. Tri- and polyatomic monobasic Acids.

Just as the glycols yield in the first instance diatomic monobasic acids upon oxidation, compounds which possess at the same time the characters of a monatomic alcohol and a monobasic acid, so are the polyatomic alcohols at first converted (by cautious oxidation in the air in presence of platinum black, or also by means of nitric acid), into monobasic acids, which likewise retain the characteristics of a mono-, di-, tri-, etc. atomic alcohol, *i.e.* into tri-, etc. atomic monobasic acids. These correspond entirely with lactic acid in behaviour, but, as alcohols, are polyatomic.

Since the oxidation consists in the conversion of a $—CH_2.OH$ group into carboxyl, the resulting acids consequently contain as many hydroxyls as the original alcohols, this number being again expressed by the designation "tri-, tetra-, etc. atomic monobasic acids." The number of alcoholic hydroxyls in the molecule is determined—as in the case of the polyatomic alcohols—by the number of acetyl groups which can be introduced upon treatment with acetic anhydride.

The law which applies to the polyatomic alcohols, viz., that only one hydroxyl can be bound to one atom of carbon, also holds good for the alcohol-acids. Their carbon-atom chain is the same as that of the mother compound.

Most of the compounds belonging to this class either crystallize badly or are gum-like. A number of these acids also result from the cautious oxidation of the sugars or of the unsaturated acids, $C_nH_{2n-2}O_2$ (see p. 179). Many of them yield lactones.

I. Triatomic Monobasic Acids.

Glyceric acid *(Propane-diolic acid)*, $C_2H_3(OH)_2(CO_2H)$, **is a syrupy liquid which results from the cautious oxidation of**

glycerine. It is optically inactive. A *d*-rotatory modification is also known.

Its alcoholic amine is **Serine**, $C_2H_3(OH)(NH_2)(CO_2H)$, a compound which resembles glycocoll, and which is formed by boiling silk-gum with dilute sulphuric acid.

Di-oxy-stearic acid, $C_{18}H_{34}(OH)_2O_2$, is produced by the cautious oxidation of oleic acid, just as glycerine is from allyl alcohol.

II. Tetratomic Monobasic Acids.

Erythritic acid (*Butane-triolic acid*), $C_3H_4(OH)_3(CO_2H)$, results from the cautious oxidation of erythrite and of levulose.

III. Pentatomic Monobasic Acids.

Pentonic acids (*Pentane-tetrolic acids*), $C_4H_5(OH)_4(CO_2H)$. Three stereo-isomeric forms of these are known, viz. *Arabonic*, *Ribonic* and *Xylonic acids* (B. **24**, 4215).

Arabonic acid, $C_4H_5(OH)_4(CO_2H)$, results from the oxidation of arabinose; it undergoes transformation into its stereo-isomer, *Ribonic acid*, when heated with pyridine.

Saccharic acid (*Hexane-tetrolic acid*), $C_5H_7(OH)_4(CO_2H)$, is obtained by the action of lime on grape and fruit sugars.

Its isomers, **Iso-** and **Meta-Saccharic acids**, result in an analogous manner from milk sugar. These acids are only known in the form of salts and of lactones, the latter being termed *Saccharines*, $C_6H_{10}O_5$ (**Saccharine**, **Iso-Saccharine**, and **Meta-Saccharine**); they crystallize well, and are isomeric with starch, etc. (Cf. B. **17**, 1302; **18**, 2514).

IV. Hexatomic (etc.) Monobasic Acids.

Hexonic acids (*Hexane-pentolic acids*), $C_5H_6(OH)_5(CO_2H)$. These acids are of particular importance, on account of their close connection with the sugar varieties. They are obtained either by the cautious oxidation of the corresponding sugars, *e.g.* by means of bromine water; or by the reduction of the corresponding dibasic acids (saccharic acid, etc.); or, lastly, through the taking up of hydrocyanic acid by the pentoses, just as lactic acid is formed from aldehyde. Conversely, the hexonic acids—in so far as lactones of these are known—are on the one hand reconverted into the sugars, by reducing the lactones with sodium amalgam; while, on the other hand, they are oxidized by nitric acid to the corresponding dibasic acids.

We have the following relations:—

Mannonic acid	Mannose	Mannite.
Gluconic acid	Glucose	Sorbite.
Gulonic acid	Gulose	
Galactonic acid	Galactose	Dulcite.
Talonic acid	Talose	

Some of the hexonic acids are only known in the form of their lactones. The phenyl-hydrazines are frequently made use of for their isolation.

Investigation has shown that those acids all possess the same constitutional formula,

$$CH_2OH—CHOH—CHOH—CHOH—CHOH—CO_2H,$$

and that they are therefore structurally identical. The differences between them are explained by the theory of the asymmetric carbon atom,—the acids are stereo-isomeric,—just like the corresponding sugar varieties (which see). And just as the latter exist in several optically different modifications (which are distinguished as dextro-, lævo-, or inactive, according as they correspond to *d*-, *l*-, or *i*-glucose), so do the several hexonic acids (with the exception of talonic), these being likewise characterized as dextro-, lævo-, or inactive, according to their genetic relations. Theoretically 16 such stereo-isomers can exist, and the greater number of them are known. By the conversion of the hexonic acids (through the hexoses) into the corresponding alcohols (mannite, etc.), the number of possible stereo-isomers is diminished, since an asymmetric carbon atom is thereby rendered symmetrical. And, further, when the hexonic acids are transformed into the dibasic acids, a similar diminution is observed.

When heated with quinoline and a little water, some of the hexonic acids pass partially into other acids of the same class, a state of equilibrium being reached; for instance, *d*-mannonic acid into *d*-gluconic, galactonic acid into talonic, and *vice versa.* The inactive acids can be split up into their optically active isomers by means of the strychnine salts, *e.g.* *i*-mannonic and *i*-galactonic acids. The racemic or inactive modification

crystallizes from mixtures of the *d*- and *l*- modifications in aqueous solution (but not in every case); see B. **25**, 1025. *l*-Gluconic and *l*-mannonic acids result simultaneously from arabinose by the taking up of hydrocyanic acid by the latter ("arabinose-carboxylic acids"); they are therefore stereoisomeric, in respect to the carbon atom by which this synthesis is effected.

From the hexoses, heptoses, etc., a number of alcohol-acids have been similarly prepared, *e.g.*:—

Gluco-heptonic acid (Glucose-carboxylic acid), $C_6H_7(OH)_6(CO_2H)$;
Rhamno-hexonic acid, $C_6H_8(OH)_5(CO_2H)$, from rhamnose, etc.

C. Aldehyde-alcohols.

1. **Glycollic aldehyde** (*Ethanolal*), $CH_2(OH)—CHO$. This is only known in aqueous solution. Reduces Fehling's solution in the cold (B. **25**, 2552).

2. **Aldol**, $CH_3—CH(OH)—CH_2—CHO$. A condensation product of aldehyde, see p. 145 (*Wurtz*). It forms a thick liquid, easily soluble in water.

3. **Glyceric aldehyde**, $CH_2(OH)—CH(OH)—CHO$, is the aldehyde of glyceric acid, and is obtained by very careful oxidation of glycerine. It is only known in solution. It acts as a powerful reducing agent, and is changed into a sugar by condensation. (See Acrose.)

The **Sugars** are also to be looked upon as aldehyde-alcohols or ketone-alcohols; they will be treated of separately (p. 307).

D. Ketone-alcohols (Ketols).

Acetone-alcohol (*Propanolone*), *acetol*, *acetyl-carbinol*, $CH_3—CO—CH_2.OH$. Colourless liquid, which boils at 147° with some decomposition. Is prepared from monochloro-acetone and barium carbonate; also by fusing grape sugar, etc., with potash (B. **16**, 837). It reduces *Fehling's* solution even in the cold.

Dimethyl-ketol (2-3-*Butanolone*), $CH_3—CO—CH(OH)—CH_3$, B. Pt. 141°–142°, is obtained by reducing di-acetyl, $CH_3—CO—CO—CH_3$. It is a colourless liquid, miscible with water, and it reduces Fehling's solution at the ordinary temperature. **Aceto-propyl alcohol**, $CH_3—CO—CH_2—CH_2—CH_2OH$ (B. **22**, 1196), and **Aceto-butyl alcohol**, $CH_3—CO—(CH_2)_3—CH_2OH$ (B. **21**, 735), are homologues of it. Further, **Aceto-isopropyl alcohol**, $CH_3—CO—CH_2—CH(OH)—CH_3$, which results from the condensation of aldehyde with acetone (by means of aqueous alkali); liquid, B. Pt. 177°. This last gives up water and passes into **Ethylidene-acetone**, $CH_3—CO—CH=CH—CH_3$ (liquid; B. Pt. 122°).

E. Diatomic Aldehydes.

Glyoxal (*Ethane-dial*), CHO—CHO (*Debus*, 1856). Formed by the cautious oxidation of alcohol or, better, of aldehyde. White deliquescent mass. Possesses all the characteristic properties of aldehydes; being a diatomic aldehyde, its bisulphite results from 1 mol. glyoxal and 2 mols. $NaHSO_3$, and it yields a di-cyanhydrin. Concentrated ammonia converts it into **Imidoazole** (p. 333).

F. Diatomic Ketones.

1. **Di-acetyl** (*Butane-dione*), *a-diketo-butane*, CH_3—CO—CO—CH_3, B. Pt. 87°–88°. This can be prepared by boiling iso-nitroso-methyl acetone, CH_3—CH(N.OH)—CO—CH_3 (p. 157), with dilute H_2SO_4, the oxime group being exchanged here for oxygen. Yellow-green liquid, its vapour having the colour of chlorine, and an odour similar to that of quinone (*v. Pechmann*, B. **20**, 3162; **24**, 3954; *Fittig* and his pupils, A. **249**, 182). Reduction converts it into dimethyl-ketol. Homologues are known (cf. B. **22**, 2115).

2. **Aceto-acetone**, CH_3—CO—CH_2—CO—CH_3, is formed by the action of Al_2Cl_6 upon acetyl chloride, or better (B. **22**, 1009), by the action of sodium upon a mixture of acetic ether and acetone (see Aceto-acetic ether synthesis, p. 241):—

$$CH_3—CO.OC_2H_5 + CH_3—CO—CH_3 =$$
$$CH_3—CO—CH_2—CO—CH_3 + C_2H_5OH.$$

It is a liquid which boils at 137°.

3. **Acetonyl-acetone**, *γ-di-keto-hexane*, CH_3—CO—CH_2—CH_2—CO—CH_3. Prepared from monochlor-acetone and aceto-acetic ether (B. **17**, 2756); also from diaceto-succinic ether (B. **22**, 168, 2100). It forms a liquid of pleasant odour, B. Pt. 188°.

These three compounds are the simplest representatives of the *a*-, *β*-, and *γ*-diketones, *i.e.* of those diketones whose carbonyl (or keto-) groups are either next to one another (*a*-position), or separated by one carbon atom (*β*-position), or separated by two (*γ*-position). (The ketols may be classified in the same way as *a*-, *β*-, and *γ*-ketols.)

As diketones they yield (*e.g.*) mono- and di-oximes, and also mono- and di-hydrazones. Such hydrazones, and also those from the di-aldehydes, *e.g.*

$$\begin{array}{l} CH_3—C{=}N—NH—C_6H_5 \\ \quad\quad\;| \\ CH_3—C{=}N—NH—C_6H_5 \end{array}$$

Diacetyl-dihydrazone,

are termed *Osazones;* thus diacetyl-dihydrazone is diacetyl-osazone. They also frequently result from the action of hydrazines upon ketone-alcohols, or aldehyde-alcohols, an atom of oxygen being at the same time taken up; they are mostly yellow in colour (cf. the phenyl-hydrazine compounds of the carbohydrates).

The diketones show the most varied behaviour on condensation. By the action of alkali on the α-diketones, they yield benzene derivatives (see Quinone); the β-diketones readily pass into pyrazole and isoxy-azole derivatives, and serve for the synthesis of derivatives of quinoline; while the γ-diketones are easily converted into derivatives of pyrrol, furfurane, and thiophene.

The constitution of the above compounds is usually deduced directly from their mode of formation.

G. Oxy-methylene-ketones and Ketone-aldehydes.

Oxy-methylene-acetone, $CH(OH)=CH—CO—CH_3$, a derivative of vinyl alcohol (p. 96), is obtained as sodium salt by the action of acetone upon ethyl formate in the presence of sodic ethylate (a "condensation" analogous to the formation of aceto-acetic ether (p. 241). It is, however, only capable of existing in the free state for a short time, after which it polymerizes into triacetyl-benzene, just as acetone does to mesitylene (cf. B. 21, 1144; 22, 3273). This compound was formerly considered to be *Aceto-acetic aldehyde*, $CH_3—CO—CH_2—CHO$, *i.e.* the aldehyde of aceto-acetic acid (p. 243); B. 25, 1040, 1780.

Pyroracemic Aldehyde, *methyl-glyoxal*, $CH_3—CO—CHO$, can be prepared from isonitroso-acetone, just as di-acetyl can from methyl-isonitroso-acetone.

H. Monobasic Aldehyde- and Oxy-methylene Acids.

Glyoxalic acid (*Ethanalic acid*), *glyoxylic acid*, $CHO—CO_2H$ (or $CH(OH)_2—CO_2H$), occurs in unripe fruits such as grapes, gooseberries, etc., and may be prepared, *e.g.*, by superheating dichlor-acetic acid, $CHCl_2—CO_2H$, with water, Cl_2 being here exchanged for O or 2(OH). It crystallizes in rhombic prisms, easily soluble in water, and is volatile with steam. The acid

and most of its salts contain 1 mol. H_2O, which points to the formula $CH(OH)_2—CO_2H$, analogous to that of chloral hydrate, from which it is derivable by the exchange of 3Cl for O and OH.

Glycuronic acid, $CHO—[CH(OH)]_4—CO_2H$. The lactone of this acid forms colourless crystals, which melt at about 175°. The acid itself is obtained from saccharic acid by reduction with sodium amalgam. It is found as camphor compound in the urine of dogs after they have had camphor administered to them.

β-Oxy-acrylic acid, *Oxy-methylene-acetic acid*, $CH(OH)=CH—CO_2H$, is formed as ether by the action of sodium upon a mixture of ethyl formate and acetate (see p. 241). It is readily condensible to trimesic acid (p. 354). It used to be regarded as *Formyl-acetic acid*, $CHO—CH_2—CO_2H$, the semi-aldehyde of malonic acid (cf. B. 25, 1042).

I. Monobasic Ketonic Acids.

Ketonic acids are compounds which possess at one and the same time the properties of acids and ketones; thus, besides being capable of forming salts, ethers, etc., they also combine with sodium bisulphite, yield oximes with hydroxylamine hydrochlorate (see p. 155), are reduced by nascent hydrogen to secondary alcohol-acids, and so on. The most important members of this class are pyroracemic acid, $CH_3—CO—CO_2H$, aceto-acetic acid, $CH_3—CO—CH_2—CO_2H$, and levulinic acid, $CH_3—CO—CH_2—CH_2—CO_2H$.

Constitution and *Nomenclature.* The ketonic acids are characterized theoretically by the presence of carboxyl and of carbonyl, the latter being linked to carbon on both sides. They may be derived from the monobasic fatty acids in such manner that one hydrogen atom of the radicle of the latter is replaced by an acid radicle R—CO— (in the cases above-mentioned by $CH_3—CO$, acetyl), as the name aceto-acetic acid indicates. Levulinic acid is therefore β-aceto-propionic acid, and pyroracemic acid is aceto-formic acid; or, the ketonic acids are derived from the fatty acids by the replacement of the two hydrogen atoms of a $CH_2—$ group by an atom of oxygen.

In the latter case aceto-acetic acid (for instance) is to be designated *β-Keto-butyric acid* (this being analogous to the nomenclature of the oxy-acids, p. 223), or with the "O.N." *3-Butanonic acid.*

The *constitution* of the ketonic acids is as a rule easy to determine, either from the mode of their synthesis, or from their transformation into the

corresponding alcohol-acids—(oxy-acids)—of known constitution, by means of nascent hydrogen, and so on.

For the constitution of aceto-acetic ether, cf. also p. 244; for that of the γ-ketonic acids, cf. B. **23**, Ref. 396.

Modes of Formation.

1. α-Ketonic acids result upon saponifying the cyanides of the acid radicles (*Claisen, Shadwell*), (cf. p. 191):—

$$\underset{\text{Acetyl cyanide.}}{CH_3—CO—CN} + 2H_2O = \underset{\text{Pyroracemic acid.}}{CH_3—CO—CO_2H} + NH_3$$

This method of formation gives the constitution.

2. Aceto-acetic and other β-ketonic acids are obtained in the form of compound ethers by the action of sodium or sodium ethylate upon acetic and homologous ethers:—

$$2(CH_3—CO.OC_2H_5) = CH_3—CO—CH_2—CO.OC_2H_5 + C_2H_5OH.$$

According to *Claisen* and *Lowman* (B. **20**, 651), the acetic ether is first converted by the sodium ethylate (which is also formed in small quantity by a secondary reaction when sodium is employed) into an addition compound: $CH_3—C \begin{cases} O.C_2H_5 \\ O.C_2H_5 \\ ONa \end{cases}$, a derivative of ortho-acetic acid (p. 214), which then reacts with another molecule of acetic ether, thus:—

$$CH_3—C(OC_2H_5)_2(ONa) + CH_3—CO—OC_2H_5 =$$
$$\underset{\text{Sodio-aceto-acetic ether.}}{CH_3—CO—CHNa—CO.OC_2H_5} + 2C_2H_5OH.$$

From the sodium salt thus obtained, the aceto-acetic ether can be liberated by acetic acid.

As shown in the above formation of aceto-acetic ether, one molecule of acetic ether reacts upon a second molecule. Many reactions of an analogous nature, in which the two reacting molecules consist of different ethers, may be brought about in the same way by the aid of sodium ethylate or sodium (*Wislicenus*, A. **246**, 306). Thus oxalic and acetic ethers coalesce to oxalo-acetic ether, the ether of a dibasic ketonic acid:—

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + CH_3.COOC_2H_5 = COOC_2H_5.CO.CH_2.CO.OC_2H_5 + C_2H_5OH.$$

Further, compound ethers readily react with ketones, with the formation of di-ketones (*L. Claisen*):—

$$CH_3.CO.OC_2H_5 + CH_3-CO-CH_3 = \underbrace{CH_3-CO-CH_2-CO-CH_3}_{\text{Aceto-acetone.}} + C_2H_5.OH.$$

When ethyl formate is employed, ketonic aldehydes do not result, but their structural isomers oxy-methylene compounds (p. 239); with acetone, for example, oxy-methylene-acetone, thus:—

$$\underbrace{H-CO.OC_2H_5}_{\text{Ethyl formate.}} + CH_3-CO-CH_3 = \underbrace{CH(OH)=CH-CO-CH_3}_{\text{Oxy-methylene-acetone.}} + C_2H_5.OH.$$

3. Higher homologues of aceto-acetic ether (β-ketonic acids) are easily obtained from it by the action of sodium ethylate and halogen-alkylene (p. 245).

4. Ketonic acids are produced by the cautious oxidation of secondary alcohol-acids:—

$$\underbrace{CH_3-CH(OH)-CO.OH}_{\text{Lactic acid.}} + O = \underbrace{CH_3-CO-CO.OH}_{\text{Pyroracemic acid.}} + H_2O.$$

5. Special modes of formation are given below.

Behaviour. (See also above.)

1. While the α- and γ-ketonic acids are stable liquids, some of them *even withstanding distillation, the β-ketonic acids are exceedingly unstable* in the free state, breaking up very readily into the corresponding ketone and carbon dioxide.

2. Reduction converts the ketonic acids into secondary alcohol-acids; in *the case, however, of the γ-ketonic acids, γ-lactones are produced instead of* alcohol-acids, water being separated.

3. In the ethers of the β-ketonic acids, one hydrogen atom is readily replaceable by a metal; thus, aceto-acetic ether and sodium ethylate yield sodio-aceto-acetic ether, $C_4H_4NaO_3(C_2H_5)$. Its behaviour with halogen-alkyl (see p. 245) shows that the replaceable hydrogen atom comes from the methylene group, as shown by the formula: $CH_3-CO-CHNa-CO.OC_2H_5$.

This capability of replacement is explained by the acidifying influence exerted by the two carbonyl groups which are linked directly to the methylene, *i.e.* the carbonyl of the group CH_3-CO-, and that of the group $-CO.OH$. [Cf. the relation of hydrated carbonic acid, $CO(OH)_2$, to (two molecules of) water, $2H(OH)$.]

4. For the synthesis of the higher β-ketonic acids; and

5. For the decomposition of the β-ketonic acids, with production of ketones or of acids, see Aceto-acetic ether.

6. The ketonic acids show the most varied condensation reactions; with aniline the β-ketonic acids yield quinoline derivatives, and with phenyl hydrazine, derivatives of pyrazole.

Pyroracemic acid, $C_3H_4O_3$, $= CH_3-CO-CO_2H$, is a liquid which is readily soluble in water, alcohol and ether, boils with slight decomposition at 165°–170°, and smells of acetic acid and extract of beef.

Formation. 1. By the dry distillation either of tartaric or of racemic acid, hence its name.

2. By the oxidation of lactic acid by means of $KMnO_4$.
3. By saponifying acetyl cyanide with HCl, (*Claisen, Shadwell*):

$$CH_3—CO—CN + 2H_2O = CH_3—CO—CO_2H + NH_3.$$

Pyroracemic acid has a tendency to polymerize. Its salts crystallize only with difficulty. Nascent hydrogen reduces it to ethylidene-lactic acid: $CH_3—CO—CO_2H + H_2 = CH_3—CH(OH)—CO_2H$, from which reaction and from mode of formation 3, its constitution follows. It possesses in a marked degree the ketonic property of forming condensation products, going either into derivatives of benzene, (B. **5**, 956), or—in presence of ammonia—into those of pyridine. Sulphuric acid causes it to condense with the aromatic hydrocarbons, just as in the case of the ketones, (B. **14**, 1595).

Cystine, $C_6H_{12}N_2S_2O_4$, the disulphide of amido-thio-lactic acid or **cysteïne**, $C_2H_3(NH_2)(SH)CO_2H$, is to be regarded as a derivative of pyroracemic acid, (see ethyl di-sulphide). It is found in urinary sediments and gravel, (B. **18**, 258).

α-Keto-butyric acid, *propionyl-carboxylic acid*, $CH_3—CH_2—CO—CO_2H$, resembles pyroracemic acid.

Aceto-acetic acid, *β-keto-butyric acid*, $CH_3—CO—CH_2—CO_2H$. A strongly acid liquid, miscible with water, and breaking up into acetone and carbonic acid upon warming. It is prepared by the cautious saponification of its ethyl ether, (B. **15**, 1376; 1871). Its aqueous solution is coloured violet-red by ferric chloride. The Na- or Ca-salt is sometimes contained in urine, (B. **16**, 2314). Aceto-acetic acid may also be looked upon as acetone-carboxylic acid, $C_3H_5O(CO_2H)$.

Aceto-acetic ether, $CH_3—CO—CH_2—CO_2C_2H_5$, is obtained in the form of its sodium compound, sodio-aceto-acetic ether, by the action of sodium or sodium ethylate upon ethyl acetate (see above; *Geuther*, 1863; *Frankland* and *Duppa*):

$$2CH_3—CO.OC_2H_5 + NaO.C_2H_5$$
$$= CH_3—CO—CHNa—CO.OC_2H_5 + 2C_2H_5OH.$$

The ether is obtained from the sodium compound upon the addition of acid. It is a liquid of neutral reaction, boiling at

181°, only slightly soluble in water but easily in alcohol and ether, and of a pleasant fruity odour. Ferric chloride colours its aqueous solution violet-red. It is split up upon being boiled with alkali, dilute aqueous alkali or baryta water (or also dilute sulphuric acid) producing mainly carbon dioxide, acetone and alcohol ("ketonic decomposition"):

$$CH_3—CO—CH_2—CO_2(C_2H_5) + H_2O$$
$$= CH_3—CO—CH_3 + CO_2 + HO.C_2H_5;$$

very concentrated alcoholic potash, however, produces chiefly (2 mols.) acetic acid; ("acid decomposition," *Wislicenus*):

$$CH_3—CO—CH_2—CO_2(C_2H_5) + 2H_2O$$
$$= 2CH_3—CO.OH + HO.C_2H_5.$$

The constitution of aceto-acetic ether follows from its formation and behaviour. Besides the formula:—

$$\text{(I.)}\ CH_3—CO—CH_2—CO.OC_2H_5,$$

we have also to take into consideration that of β-oxy-isocrotonic ether:—

$$\text{(II.)}\ CH_3—C(OH)=CH—CO.OC_2H_5.$$

A comparison with β-oxy-acrylic ether (p. 240), in which the presence of the oxy-methylene group, —C(OH), has been proved, is a decisive argument in favour of formula I. (see B. 25, 1041, 1176). On the other hand, the sodium compound of aceto-acetic ether comports itself with several reagents as if it were derived from formula II., the "*pseudo-form*" of the ester, and as if it possessed the constitution $CH_3—C(ONa)= CH—CO_2C_2H_5$. Unless, therefore, those reactions are to be regarded as abnormal, sodio-aceto-acetic ether must be held to possess both formulæ, *i.e.* to be *tautomeric;* see Cyanogen compounds, section F.

One atom of hydrogen in aceto-acetic ether is easily replaceable by metals (*Geuther; Conrad*, A. 188, 269). The sodium salt results with evolution of hydrogen upon the addition of sodium, and also upon mixing the alcoholic solution of the

ether with the calculated amount of sodium dissolved in absolute alcohol:

$$C_4H_5O_3(C_2H_5) + C_2H_5.ONa = C_4H_4NaO_3(C_2H_5) + C_2H_5.OH.$$

In agreement with this the ether dissolves in dilute alkali, being again separated from the solution by the addition of acid.

Sodio-aceto-acetic ether, $CH_3—CO—CHNa—CO_2C_2H_5$; long needles or a faintly lustrous loose white mass. **Copper salt**: bright green needles.

The metal in sodio-aceto-acetic ether is readily replaced by an alcohol radicle by the action of iodo- or bromo-alkyl, sodium iodide or bromide being formed at the same time. We thus obtain alkylated aceto-acetic ethers, *e.g.*:

Methyl-aceto-acetic ether or **Ethylic methyl-aceto-acetate**, $CH_3—CO—CH(CH_3)—CO_2(C_2H_5)$, and the corresponding **Ethyl-** and **Propyl-aceto-acetic ethers**, etc. In these compounds the H may be again replaced by Na, and this again substituted by alkyl, with the production of di-alkylated aceto-acetic ethers, *e.g.*: **Dimethyl-aceto-acetic ether** or **Ethylic dimethyl-aceto-acetate**, $CH_3\text{-}CO\text{-}C(CH_3)_2\text{-}CO_2(C_2H_5)$; **Methyl-ethyl-aceto-acetic ether**, $CH_3\text{-}CO\text{-}C(CH_3)(C_2H_5)\text{-}CO_2(C_2H_5)$, and so on.

These alkylated aceto-acetic ethers exactly resemble their mother substance, especially in that they undergo either the "ketonic decomposition" or the "acid decomposition," according to their degree of concentration, upon treatment with alkalies; the latter decomposition also upon treatment with dilute acids, (see above, also A. **190**, 275). The first-named decomposition leaves the substituting alcohol radicles in the acetone residue of the molecule, and the last-named in one of the two resulting acid molecules, *i.e.*, there are formed either alkyl-acetones (homologues of acetone), or alkyl-acetic acids (homologues of acetic acid). We have thus at command here a most excellent method for the synthesis of any simple or double alkyl ketone or acid:

$$1.\ CH_3—CO—CRR'—CO_2C_2H_5 + H_2O = CH_3—CO—CHRR' + HO.C_2H_5 + CO_2;$$

$$2.\ CH_3—CO—CRR'—CO_2C_2H_5 + 2H_2O = CH_3—CO.OH + CHRR'—CO_2H + HO.C_2H_5.$$

(RR' = alcohol radicles. Cf. *Wislicenus* and his pupils, A. **186**, 161.)

In a perfectly analogous manner we can introduce acid instead of alkyl radicles into aceto-acetic ether, and thereby give rise to the most various compounds, *e.g.*, from acetyl chloride, **di-aceto-acetic ether**, $(CH_3—CO)_2CH—CO_2(C_2H_5)$; from chloro-carbonic ether, $Cl—CO_2C_2H_5$ (p. 290), chiefly a mixed carbonic ether, $CH_3—C(O.CO_2C_2H_5)=CH.CO_2C_2H_5$, derived from the pseudo-form of sodio-aceto-acetic ether (p. 244), but also **aceto-malonic ether**, $(CH_3—CO)—CH(CO_2C_2H_5)_2$; from monochlor-acetic ether, $CH_2Cl—CO_2(C_2H_5)$, **aceto-succinic ether**, $CH_3—CO—CH(CH_2—CO_2C_2H_5)(CO_2C_2H_5)$ (see Malonic and Succinic acids, and also the Synthesis of dibasic acids), etc. Iodine acts upon sodio-aceto-acetic ether to produce **di-aceto-succinic ether**, which is interesting from its transformations, thus:

$$\begin{matrix} CH_3\text{-}CO\text{-}CHNa\text{-}CO_2C_2H_5 \\ CH_3\text{-}CO\text{-}CHNa\text{-}CO_2C_2H_5 \end{matrix} + I_2 = \begin{matrix} CH_3\text{-}CO\text{-}CH\text{-}CO_2C_2H_5 \\ | \\ CH_3\text{-}CO\text{-}CH\text{-}CO_2C_2H_5 \end{matrix} + 2NaI.$$

Chlor- and Dichlor-aceto-acetic ethers, which are very active chemically, are produced by the replacement of the H of the methylene group by Cl. The two methylene hydrogen atoms are also replaceable by the iso-nitroso group, =N—OH (by the action of N_2O_3), and by the imido group, =NH (cf. A. **226**, 294).

Levulinic acid, $C_5H_8O_3$, = $CH_3—CO—CH_2—CH_2—CO_2H$. Plate crystals, M. Pt. 33°, B. Pt. 239°. Results from the action of acids upon cane sugar, lævulose, cellulose, gum, starch and other carbo-hydrates (A. **175**, 181; **206**, 207), and has also been prepared synthetically. For its constitution, cf. A. **256**, 314. It is employed in cotton printing, and for the preparation of anti-thermine (which see), etc.

X. DIBASIC ACIDS.

Dibasic acids are those which are capable of forming two series of salts, acid and neutral, with monatomic bases, and likewise two series of ethers, chlorides, amides, etc. The dibasic acids proper are characterized theoretically by the presence of two carboxyls in the molecule.

These acids may either possess the acid character pure and simple, or also at the same time the character of an alcohol, *e.g.* lactic acid; in the latter case they still contain alcoholic hydroxyl. A distinction is drawn between diatomic dibasic and tri-, tetra-, etc. atomic dibasic acids. They may be either saturated or unsaturated compounds. Lastly, they may also be at the same time acid and aldehyde, or ketone, etc. The dibasic carbonic acid will be treated of later on (p. 287 *et seq.*).

A. Saturated diatomic dibasic Acids, $C_nH_{2n-2}O_4$.

Oxalic	acid,	$C_2H_2O_4$	Suberic	acid,	$C_8H_{14}O_4$
Malonic	,,	$C_3H_4O_4$	Lepargylic,	,,	$C_9H_{16}O_4$
Succinic	,,	$C_4H_6O_4$	Sebacic	,,	$C_{10}H_{18}O_4$
Pyrotartaric	,,	$C_5H_8O_4$	Brassylic	,,	$C_{11}H_{20}O_4$
Adipic	,,	$C_6H_{10}O_4$	Rocellic	,,	$C_{17}H_{32}O_4$
Pimelic	,,	$C_7H_{12}O_4$	Dicetyl-malonic	,,	$C_{35}H_{68}O_4$

Oxalic acid is to be considered as the isolated group carboxyl, $(CO.OH)_2$. Its homologues are di-carboxylic acids of the paraffins; thus, malonic is methane-di-carboxylic acid, $CH_2(CO_2H)_2$, etc.

The above are solid crystalline compounds of strongly acid character, and most of them are readily soluble in water. Upon heating, they either yield an anhydride or carbon dioxide is given off; but most of them can be volatilized *in vacuo.*

Formation.—1. By the oxidation of the di-primary glycols. (See table, p. 220.)

1*a*. By the oxidation of primary oxy-acids and, generally, of many complex compounds, such as fats, fatty acids and carbohydrates.

2. By the saponification of the corresponding nitriles; thus, oxalic acid is formed from cyanogen, and succinic acid from ethylene cyanide:

$$C_2N_2 + 4H_2O = C_2O_4H_2 + 2NH_3.$$
$$C_2H_4(CN)_2 + 4H_2O = C_2H_4(CO_2H)_2 + 2NH_3.$$

Since ethylene cyanide is a glycol derivative, its conversion into succinic acid represents the synthesis from a glycol of an acid containing two atoms of carbon more than itself, *i.e.* the exchange of 2(OH) for $2(CO_2H)$, or the indirect combination of ethylene with $2CO_2H$.

2*. By the saponification of the cyano-fatty acids (p. 185), and consequently of the haloid fatty acids also. Thus chlor- or cyan-acetic yields malonic acid, β-iodo- (or cyano-) propionic, common succinic acid, and α-iodo- (or cyano-) propionic, ethylidene-succinic acid.

A dibasic acid can therefore be formed from each oxy-acid by the exchange of OH for CO_2H, or indirectly from a fatty acid by the replacement of H by CO_2H.

3. The homologues of malonic acid can be prepared from malonic acid itself by a reaction exactly analogous to the aceto-acetic ether synthesis (the "malonic ether synthesis," p. 253).

3*. The dibasic acids are also obtained by means of the aceto-acetic ether synthesis. Aceto-malonic and aceto-succinic acids, which have already been mentioned at p. 246, yield respectively malonic and succinic acids by the separation of acetyl ("acid decomposition").

4. Higher homologues are obtainable by the electrolysis of the ester potassium salts (p. 251) of the simpler acids, *e.g.* adipic acid from the ester potassium salt of succinic:—

$$2CO_2C_2H_5—CH_2—CH_2—CO_2K + 2H_2O$$
$$= CO_2C_2H_5—(CH_2)_4—CO_2C_2H_5 + 2KHCO_3 + H_2.$$

5. For further modes of preparation, see under Succinic acid.

The *Constitution* of the acids $C_nH_{2n-2}O_4$ is as a rule very easy to determine from the above-mentioned modes of formation, especially 2 and 3. According to these, one has to decide between the malonic acids proper, *i.e.* malonic acid and its alkylated derivatives (p. 252), whose two carboxyl groups are both linked to one carbon atom:

$$CH_2(CO_2H)_2, \qquad R—CH(CO_2H)_2, \qquad RR'C(CO_2H)_2,$$

and ordinary succinic acid and its homologues, which contain the carboxyls bound to two different carbon atoms.

The divalent acid residues, C_2O_2 = "oxalyl," $C_3H_2O_2$ = "malonyl," and $C_4H_4O_2$ = "succinyl," which are combined with the two hydroxyls, are termed the *radicles* of the dibasic acids.

Isomers.—Isomers of oxalic and malonic acids are neither theoretically possible nor actually known. We know, however, two succinic acids, viz., $\begin{matrix} CH_2—CO.OH \\ \dot{C}H_2—CO.OH \end{matrix}$ and $CH_3—CH(CO_2H)_2$. The former corresponds to ethylene chloride and the latter to ethylidene chloride, from which they are respectively

derived by the exchange of two chlorine atoms for two carboxyls. Hence the names, ethylene- and ethylidene-succinic acids.

Since ethylene cyanide can be prepared from the chloride, the above derivation of ethylene-succinic acid is also an experimental one; this is not the case however with the isomeric acid, since, speaking generally, when several chlorine atoms are bound to the same carbon atom, as in ethylidene chloride, they cannot be exchanged for cyanogen.

Behaviour.—Those of the dibasic acids whose carboxyls are attached to different carbon atoms yield intra-molecular anhydrides by the separation of a molecule of water. These anhydrides result in part by direct heating, in part by the action of phosphorus pentachloride, acetyl chloride or carbon oxy-chloride upon the acids, (B. **10**, 1881; **17**, 1285). They recombine slowly with water to the hydrates. This formation of anhydride is favoured by the presence of methyl groups in the molecule (B. **23**, 101, 620).

The "malonic acids," on the other hand, lose CO_2 on being heated, and yield monobasic fatty acids, malonic acid itself giving acetic acid. Similarly oxalic acid breaks up into CO_2 and formic acid. (Compare the analogous formation of CH_4 from $CH_3—CO_2H$.) The derivatives of the dibasic acids, *i.e.* their ethers, amides, etc., show precisely the same characteristics as the analogous derivatives of the monobasic acids, especially in the readiness with which they are saponified.

Summary.

Derivatives.	Salts.	Ethers.	Chlorides.	Amides.
Acid.	$C_2O_2\begin{cases}ONa\\OH\end{cases}$ Acid sodium oxalate.	$C_2O_2\begin{cases}OC_2H_5\\OH\end{cases}$ Ethyl-oxalic acid.	$C_2O_2\begin{cases}Cl\\O(H)\end{cases}$ (only known in derivatives).	$C_2O_2\begin{cases}NH_2\\OH\end{cases}$ Oxamic acid.
Neutral.	$C_2O_2\begin{cases}ONa\\ONa\end{cases}$ Neutral sodium oxalate.	$C_2O_2\begin{cases}OC_2H_5\\OC_2H_5\end{cases}$ Oxalic ester.	$C_2O_2\begin{cases}Cl\\Cl\end{cases}$ Oxalyl chloride.	$C_2O_2\begin{cases}NH_2\\NH_2\end{cases}$ Oxamide.

As in the case of the glycols, complications only ensue here either where mixed derivatives exist, such *e.g.* as are partly ether and partly amide (as in the case of ethyl oxamate, p. 252), or on account of many of the acids being capable of forming imides.

Such imides are derived from the hydrogen-ammonium salts of the acids by the elimination of two molecules of water, thus:

$$\underbrace{C_2H_4 < \begin{matrix} CO.OH \\ CO.OH \end{matrix}}_{\text{Succinic acid.}} + NH_3 - 2H_2O = \underbrace{C_2H_4 < \begin{matrix} CO \\ CO \end{matrix} > NH.}_{\text{Succinimide.}}$$

Like the amides they are easily saponifiable, (cf. succinimide).

Oxalic acid ("O.N." *Ethane di-acid*), *acidum oxalicum*, $C_2H_2O_4 + 2H_2O$. This acid has been known for a very long time; it was investigated by *Scheele*.

Occurrence. In many plants, especially in Oxalis acetosella (wood sorrel), and in varieties of Rumex, as KHC_2O_4, free in varieties of Boletus, as $Na_2C_2O_4$ in varieties of Salicornia, and as calcium salt in rhubarb root, etc.

Formation. (See also p. 247):

1. By the direct combination of carbon dioxide with sodium at 360°:

$$2CO_2 + Na_2 = C_2O_4Na_2.$$

2. By raising sodium formate quickly to a high temperature:

$$2HCO_2Na = H_2 + C_2O_4Na_2.$$

3. By the oxidation of alcohol by permanganate, and of sugar, starch, wood, etc., by nitric acid, or by fusing cellulose with the hydrates of potash and soda. This last method is followed for its preparation on a large scale.

The frequency of its formation in processes of oxidation is explained by its close relation to carbonic acid, which is the final product of all oxidations.

Properties. Fine transparent monoclinic prisms which effloresce in the air. Easily soluble in water and moderately in alcohol. The anhydrous acid, which is obtained at 100°, can be sublimed, but it decomposes upon rapid heating into carbon dioxide and formic acid, or into carbon dioxide, carbon monoxide and water. The latter decomposition also takes place upon heating with concentrated sulphuric acid:

$$C_2H_2O_4 = CO_2 + CO + H_2O.$$

Oxalic acid is stable as regards nitric acid and chlorine, but permanganate of potash or manganese dioxide in acid solution oxidizes it to carbonic acid:

$$C_2H_2O_4 + O = 2CO_2 + H_2O.$$

Salts and Derivatives. The alkaline salts, acid and neutral, are readily soluble in water, the normal sodium salt being the least so. The "salt of sorrel" of commerce is a mixture of C_2O_4HK and a per-salt, $C_2O_4HK + C_2O_4H_2 + 2H_2O$, (cf. p. 165).

The calcium salt, $C_2O_4Ca + H_2O$ (or $3H_2O$), is insoluble in water and acetic acid, and serves for the recognition of oxalic acid.

Ferro-potassic oxalate, $(C_2O_4)_2FeK_2 + H_2O$, finds application in photography as a powerful reducing agent (the "oxalate developer").

Antimonic oxalate is, like tartar emetic, employed as a mordant in dyeing.

Ethyl oxalate, *oxalic ether,* $C_2O_4(C_2H_5)_2$, which can be directly prepared from its components, is liquid, while **Methyl oxalate,** $C_2O_4(CH_3)_2$, is solid, crystallizing in plates which melt at 51°; both of them possess an aromatic odour, distil without decomposition, and are easily saponifiable. Partial saponification (with one mol. KOH in alcoholic solution) produces *e.g.* **Potassium ethyl-oxalate,** $C_2O_4(C_2H_5)K$, from which the free **Ethyl-oxalic acid,** $C_2O_4(C_2H_5)H$, which is readily saponifiable, and its chloride, **Ethyl-oxalyl chloride,** $CO_2(C_2H_5)$—COCl, can easily be prepared. Oxalic ether yields, with two mols. of ammonia, oxamide, and with one mol. the mixed derivative oxamic acid, analogously to mode of formation 4 of the amides (p. 195).

Oxalyl chloride, $C_2O_2Cl_2$. From oxalic ether and PCl_5. A liquid of suffocating odour; B. Pt. 70°.

Oxamide, $C_2O_2(NH_2)_2$, the normal amide of oxalic acid, is obtained, among other methods, by the distillation of ammonium oxalate (cf. p. 194), by the partial saponification of cyanogen, and by the action of

hydrogen dioxide, H_2O_2, upon hydrocyanic acid, (B. **18**, 355). It is a white crystalline powder. As an amide it is easily saponifiable, and convertible into cyanogen by the abstraction of H_2O.

Oxamic acid, $C_2O_2(NH_2)(OH)$, the acid amide or aminic acid of oxalic acid, results from the heating of acid oxalate of ammonia. It is a crystalline powder, difficultly soluble in cold water.

Ethyl oxamate, *oxamethane*, $CO(NH_2)—CO.OC_2H_5$, (see above). Corresponding to oxamide we have **Di-methyl-oxamide**, $CO(NHCH_3)—CO(NHCH_3)$, and corresponding to oxamethane, **Ethyl-dimethyl-oxamate**, $CO(N[CH_3]_2)—CO.OC_2H_5$, both already mentioned at p. 123. PCl_5 converts oxamethane into **Cyano-carbonic ether**, $CN—CO.OC_2H_5$, a liquid of pungent odour, which is to be regarded as a semi-nitrile of oxalic acid.

Amido- and Imido-chlorides of oxalic acid are also known.

Oximide, $\begin{matrix} CO \\ | \\ CO \end{matrix}\!\!>NH$, is got by the action of PCl_5 upon oxamic acid, and forms colourless prisms easily soluble in water and of neutral reaction. It is quickly saponified by hot water, and transformed into oxamide by ammonia, (B. **19**, 3228).

Malonic acid (*Propane di-acid*), $C_3H_4O_4$, $= CH_2(CO_2H)_2$.

Occurrence. In beetroot.

Formation. (1) By the oxidation of malic acid by means of chromic acid, hence its name; (2) by the saponification of malonyl-urea (303. p), (*Baeyer*); (3) by the saponification of cyan-acetic acid, (*Kolbe*, *Müller*; A. **131**, 348; **204**, 121):

$$CH_2(CN)—CO_2H + 2H_2O = CH_2(CO_2H)_2 + NH_3.$$

Large plates or tables, readily soluble in water, alcohol and ether. M. Pt. 132°. Decomposes upon heating, as given at p. 249.

Ethyl malonate, *malonic ether*, $CH_2(CO.OC_2H_5)_2$. This ether, which is directly obtainable from cyan-acetic acid by leading HCl gas into its solution in absolute alcohol, is a liquid of faint aromatic odour boiling at 195°, and having a remarkable similarity to aceto-acetic ether. Thus the hydrogen of the methylene group is here, as in the case of the latter, replaceable by sodium, through the influence of the carbonyl groups, CO, which are also bound to the methylene; and the resulting sodio-malonic ether readily exchanges the metal for

alkyl upon treatment with alkyl iodide. By this means the higher homologues of malonic ether, *e.g.* methyl-, ethyl-, propyl- etc., malonic ethers, are obtained. Further, the second hydrogen atom in these can be exchanged in exactly the same manner for sodium and then for alkyl, whereby di-alkyl malonic acids result. This is an important method for the preparation of the higher dibasic acids, being applicable even in complicated cases; it is termed the "malonic-ether synthesis." (Cf. *Conrad* and *Bischoff*, A. **204**, 121.)

By the splitting off of CO_2 from these, the higher monobasic acids are obtained, (indirect synthesis, see p. 164, 10[a]).

Upon heating malonic ether with its sodium compound, a derivative of phloroglucin results. (See this, also B. **18**, 3454.)

Chloro-malonic ether, $CHCl(CO_2C_2H_5)_2$, a liquid boiling at 222°, is employed in analogous syntheses, and otherwise reacts in a similar way to chloracetic ether.

Succinic acids. (1) **Common Succinic acid**,* *ethylene-succinic acid, symmetrical ethane-dicarboxylic acid, acidum succinicum* (from succinum, amber), $CO_2H—CH_2—CH_2—CO_2H$. This acid has been known for a long time; its composition was determined by *Berzelius*.

Occurrence. In amber, in various resins and lignites, in many compositæ, in Papaveraceæ, in unripe wine grapes, urine, blood, etc.

Formation. (*a*) From ethylene cyanide, according to 2, p. 247; (*b*) From β-iodo- (and cyano-) propionic acid, according to 2[a]; (*c*) By the reduction of fumaric and maleic acids, $C_4H_4O_4$; (*d*) By heating its oxy-acids, malic or tartaric, with hydriodic acid, and also by certain fermentations of these, *e.g.* from the former according to the equation:

$$C_4H_5(OH)O_4 + 2HI = C_4H_6O_4 + I_2;$$

(*e*) As a bye-product in the alcoholic fermentation of sugar; (*f*) By the oxidation of fats, fatty acids and paraffins by means of nitric acid.

Preparation. From calcium malate according to *d*, by fermentation, or by the distillation of amber.

* Butane di-acid.

Properties. Monoclinic prisms or tables of an unpleasant faintly acid taste. Rather easily soluble in water. M. Pt. 185°, B. Pt. 235°. Yields succinic anhydride—(long needles) —upon distillation. For its electrolysis, see pp. 58 and 248. Is very stable towards oxidizing agents.

Of the Salts of succinic acid, the basic ferric salt, obtained by the addition of a ferric salt to ammonium succinate, is used in analysis for the separation of iron from alumina. The calcium salt is soluble in water.

The Derivatives of succinic acid correspond exactly with those of oxalic, *e.g.* **Succinamic acid**, $C_2H_4(CO_2H)(CO.NH_2)$, is analogous to oxamic acid; in this case, however, the normal chloride, **Succinyl chloride**, $C_2H_4(COCl)_2$, the analogue of acetyl chloride in all its important properties, is known (cf. B. **24**, Ref. 319). There also exists—as in the case of other dibasic acids—an imide, **Succinimide**, $C_2H_4{<}{\substack{CO\\CO}}{>}NH$. The latter crystallizes in rhombic plates, and is formed by heating acid succinate of ammonium. The basic properties of the NH_3 are so modified by the two carbonyl groups of the acid radicle that the imido-hydrogen is replaceable by metals, such as K, Ag, etc. (Cf. B. **25**, Ref. 283.)

Mono- and Di-bromo-succinic acids, $C_2H_3Br(CO_2H)_2$ and $C_2H_2Br_2(CO_2H)_2$, are easily prepared and are valuable for the syntheses of the oxy-succinic acids.

By the action of sodium upon succinic ethyl ether there is formed **succino-succinic ether**, $C_6H_6O_2(CO_2C_2H_5)_2$, a derivative of benzene.

For **Aceto- and Di-aceto-succinic ethers**, see p. 246.

(2) **Iso-succinic acid** (*Methyl-propane di-acid*), *ethylidene-succinic acid*, $CH_3—CH(CO_2H)_2$, is formed, *e.g.* by the malonic ether synthesis, or from α-chloro- (or iodo-) propionic acid (pp. 253 and 248). Needles or prisms. Decomposes upon heating into CO_2 and propionic acid, and yields no anhydride (p. 249).

Pyrotartaric acids, $C_3H_6(CO_2H)_2$. Of these four are known, this being the number theoretically possible. The two following may be mentioned here:

1. **Glutaric acid** (*Pentane di-acid*), *normal pyrotartaric acid*, $CO_2H—CH_2—CH_2—CH_2—CO_2H$, is of interest on account of its relation to piperidine; can be prepared (*e.g.*) from glutamic acid indirectly.

2. **Pyrotartaric acid** (*Methyl-butane di-acid*), *methyl-succinic acid*, $CO_2H—CH_2—CH(CH_3)—CO_2H$, results, among other

methods, along with pyroracemic acid by the dry distillation of tartaric acid, by the aceto-acetic ether synthesis, etc. Small triclinic prisms. M. Pt. 112°. Forms an anhydride.

The **higher homologues** (see Summary, p. 247) are formed along with succinic and oxalic acids by the oxidation of fats, oils, cork, etc., by means of nitric acid; adipic acid also by the oxidation of tetrahydro-α-naphthylamine. The symmetrical dialkyl-succinic acids show interesting cases of stereo-isomerism.

B. Unsaturated dibasic Acids, $C_nH_{2n-4}O_4$.

Fumaric acid, Maleic "	$C_2H_2(CO_2H)_2$.	Itaconic acid, Citraconic " Mesaconic "	$C_3H_4(CO_2H)_2$.
Hydro-muconic acid Pyro-cinchonic "	$C_6H_8O_4$.	Teraconic " etc.	$C_7H_{10}O_4$.

The unsaturated acids stand in the same relation to the saturated dibasic acids as acrylic acid does to propionic. As acids they yield derivatives analogous to those of the acids $C_nH_{2n-2}O_4$, while as unsaturated compounds they possess, in addition, the faculty of combining with two atoms of hydrogen or halogen, or with one molecule halogen hydride.

Formation. 1. By the elimination of water from the dibasic oxy-acids. Thus malic acid yields upon distillation water and maleic anhydride, which volatilizes, and also fumaric acid, which remains behind:

$$C_4H_6O_5 = C_4H_4O_4 + H_2O.$$

Citric acid yields in a similar way CO_2, H_2O, itaconic acid and citraconic anhydride.

2. By the separation of halogen hydride from the mono-haloid substitution products of succinic acid and its homologues, monobromo-succinic acid yielding fumaric, thus:

$$C_4H_5BrO_4 - HBr = C_4H_4O_4.$$

2*. From the analogous di-substitution products by the separation of the halogen.

3. Fumaric acid has been prepared synthetically from acetylene iodide, just as succinic acid has been from ethylene bromide.

The cases of *isomerism* among the acids $C_nH_{2n-4}O_4$ are of great interest.

groups, readily soluble in water and alcohol, but only slightly in ether. M. Pt. 100°. When it is distilled, maleic anhydride passes over and fumaric acid remains in the retort (p. 256).

Yields, when heated with concentrated H_2SO_4, **Cumalic acid**, $C_5H_3O_2(CO_2H)$. (*v. Pechmann*, A. **264**, 261; **273**, 164.)

Malic acid exists in several optically different modifications which correspond exactly with those of tartaric acid. The dilute solution of the natural acid is lævo-rotatory; the acid obtained from dextro-tartaric acid is dextro-rotatory; while the acid prepared from racemic, succinic, or fumaric acid is inactive, and can be separated into the active modifications.

The alkaline salts and the acid calcium salt of malic acid are readily soluble in water, while the neutral calcium salt is only sparingly soluble. As an alcohol, the acid yields ethers, *e.g.* an **Aceto-malic acid**, $C_2H_3(O.C_2H_3O)(CO_2H)_2$.

Amides and Amines of malic acid. Like glycollic acid, malic acid forms—as an acid—amides (saponifiable), and—as an alcohol—an amine (not saponifiable). The amides are:

Malamide, $C_2H_3(OH)(CO.NH_2)_2$, crystallizing in prisms, and **Malamic acid**, $C_2H_3(OH)(CO.NH_2)(CO_2H)$, the latter being known as ethyl ether. The alcoholic amine, aspartic acid, $C_2H_3(NH_2)(CO_2H)_2$, unites in itself like glycocoll the properties of a base and of an acid, but the acid character predominates. Its acid amide is asparagine.

Asparagine, $C_2H_3(NH_2)(CO.NH_2)(CO_2H)$, which is isomeric with malamide, is very widely distributed in the vegetable kingdom, being present in the young leaves of trees, in beet-root, potatoes, the shoots of peas, beans and vetches, and in asparagus; it was first found in the last-named vegetable in the year 1805. It forms glancing rhombic prisms $(+H_2O)$, easily soluble in hot water, but insoluble in alcohol and ether. Goes into aspartic acid on saponification. Is optically active.

A dextro-rotatory asparagine has likewise been obtained from the shoots of vetches (B. **20**, Ref. 510); it possesses a sweet taste, and unites with the lævo-rotatory compound to an inactive modification. For the synthesis of the asparagines and their constitution, see *Piutti*, B. **22**, Ref. 241 and 243.

Aspartic acid, $C_2H_3(NH_2)(CO_2H)_2$, **is present in beet molasses, and forms an important product of the decomposition of**

albuminoid substances by means of acids or alkalies; it has been synthetized (*e.g.*) from bromo-succinic acid and ammonia. Small rhombic tables, rather easily soluble in hot water. It exists in several optically different modifications, which differ in taste and are convertible, the one into the other (B. **20**, R. 510). Nitrous acid transforms it, as well as asparagine, into malic acid (normal amine and amide reaction).

Just as glycocoll is to be regarded as amido-acetic acid, so is aspartic acid to be looked upon as amido-succinic.

Isomers and homologues of malic acid are both possible and known.

Higher Homologues.

α- and β-Oxy-glutaric acids, Itamalic acid, Citramalic acid,	$C_3H_5(OH)(CO_2H)_2$.	Diaterebic acid,	$C_5H_9(OH)(CO_2H)_2$.
		Diaterpenylic „	$C_6H_{11}(OH)(CO_2H)_2$.
		etc.	

Glutamine, $C_3H_5(NH_2)(CO.NH_2)(CO_2H)$, and **Glutamic acid**, $C_3H_5(NH_2)(CO_2H)_2$, are the ammonia derivatives of α-oxy-glutaric acid, being homologous with asparagine and aspartic acid. The former is likewise found in beetroot and in the shoots of the vetch and gourd, while the latter is produced, together with aspartic acid and leucine, by boiling albuminous compounds with dilute sulphuric acid.

Terebic acid, $C_7H_{10}O_4$, a lactone of diaterebic acid, results from the oxidation of terpenes.

D. Tetratomic dibasic Acids.

Tetratomic dibasic acids are such as unite in themselves the properties of a diatomic alcohol with those of a dibasic acid. Theoretically they are characterized by the presence of two alcoholic hydroxyls and two carboxyls in the molecule.

The simplest possible member of the series, the compound $C(OH)_2(CO_2H)_2$, is unstable and has not the characters of an alcoholic acid, but those of the hydrate of a ketonic acid, since it contains two hydroxyls bound to the same carbon atom. (See Mesoxalic acid, p. 265.)

Tartaric acid (*Butane-diol di-acid*), *dioxy-succinic acid, oxy-malic acid*, $C_4H_6O_6$, = $C_2H_2(OH)_2(CO_2H)_2$, = $CO_2H—CH(OH)—CH(OH)—(CO_2H)$. This acid exists in four "physically isomeric" modifications (p. 39).

1. *d*- or **Dextro-tartaric acid, M. Pt. 170°;**

2. *l*- or **Lævo-tartaric acid,** *anti-tartaric acid*, M. Pt. 170°;

3. **Racemic acid,** *para-tartaric acid*, M. Pt. 206°;

4. *i*- or **Inactive tartaric acid,** *meso-tartaric acid*, M. Pt. 143°.

The two first of these acids turn the plane of polarization of light in an equal degree, but in opposite directions. By their union the inactive racemic acid is formed, and this can, conversely, be separated into its components. The fourth tartaric acid, likewise inactive, cannot be broken up in this way, but it is convertible into the other modifications.

Formation. 1. The oxidation of mannite by means of HNO_3 yields racemic acid, and that of sorbin, meso-tartaric acid.

2. The treatment of dibromo-succinic acid, $C_2H_2Br_2(CO_2H)_2$, with moist oxide of silver yields racemic and meso-tartaric acids (*Kekulé*).

3. Racemic acid results from the saponification of the cyanhydrin of glyoxal (cf. p. 238); and also upon the reduction of glyoxalic acid, two molecules of this "condensing" together.

4. The oxidation of fumaric acid by means of $KMnO_4$ yields racemic acid, and that of maleic, meso-tartaric acid (*Kekulé*).

5. When dextro- or lævo-tartaric acid is heated with some water to 170°, racemic and meso-tartaric acids are formed; meso-tartaric acid changes partially into racemic acid under analogous conditions, a state of equilibrium being reached here.

For the splitting up of racemic acid, see above.

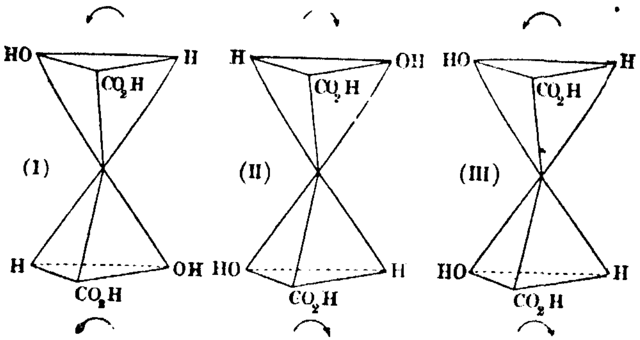
The *Constitution* of tartaric acid follows both from its relations to succinic acid (see mode of formation 2), and to glyoxal (mode of formation 3).

Isomerism of the Tartaric Acids.

Tartaric acid, CO.OH—CH(OH)—CH(OH)—CO.OH, contains according to *Le Bel* and *van 't Hoff's* theory (p. 22), two asymmetric carbon atoms, which determine the optical activity of the molecule; and this activity is connected with the spacial arrangement of the atoms or groups, H, OH and COOH, round those atoms (p. 40). This arrangement may be the same with respect to both carbon atoms, or it may be different. If it is the same, the optical action is intensified; if different, it ceases. In the former case the molecules may be either dextro-rotatory or lævo-rotatory in an equal degree (dextro- and lævo-tartaric acids); in the latter they are optically inactive (meso-tartaric acid). An inactive compound also results from

the presence (or the combination) of equal numbers of dextro- and lævo-rotatory molecules (racemic acid).

These relations may be depicted by the following figures:—

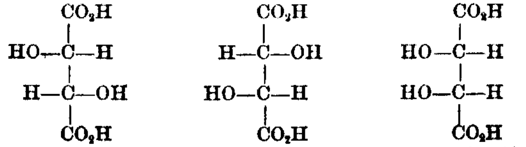


Lævo-tartaric acid. Dextro-tartaric acid. Meso-tartaric acid.

Racemic acid.

If, in Fig. II., we divide the combination of the two tetrahedra at the point which is common to both, and place the tetrahedron which was uppermost alongside of the other, the point just referred to being directed upwards, we can easily turn the latter so as to bring it into a position which shows clearly that the direction of motion of the group (OH) towards (H) and (CO_2H) is the same for both tetrahedra, viz., in the direction of motion of the hands of a watch. The same holds good for Fig. I., only in this case the analogous direction of motion for both tetrahedra is the opposite one. In Fig. III., on the other hand, the order of this succession in the upper tetrahedron, which has been lowered, is the opposite to that of the under one. If, therefore, the optical activity of the tetrahedra be dependent upon the order of succession of the substituting groups, the corresponding forces will be intensified in I. and II., but will neutralize each other in III.; the molecule III. is inactive, while I. and II. are active, although in opposite directions.

By projecting the figures on the surface of this paper we obtain the following *projection-formulæ* (*E. Fischer*, B. **24**, 2684):—



Lævo-tartaric acid. Dextro-tartaric acid. Meso-tartaric acid.

The relations between the above may be exemplified more concisely in the following manner:—

l	*d*	*l*	(*l* + *d*
|	|	|	| + |
l	*d*	*d*	*l* + *d*)
Lævo-tartaric acid.	Dextro-tartaric acid.	Meso-tartaric acid.	Racemic acid.

1. **Dextro-tartaric acid**, *acidum tartaricum*, is the tartaric acid found in nature. It was discovered by *Scheele* in 1769. It occurs in the free state or as salt, chiefly acid potassium salt, in various fruits, especially in the juice of grapes, from which bitartrate of potash or tartar—(tartarus)—separates in crystals during fermentation. When this is boiled with chalk and chloride of calcium it is transformed into the neutral lime salt, from which the acid is liberated on addition of H_2SO_4.

Large transparent monoclinic prisms, of a strong and purely acid taste, very easily soluble in water, readily also in alcohol, but almost insoluble in ether. M. Pt. 170°. Reduces an ammoniacal silver solution upon warming. When melted, it is changed into an amorphous modification, and then into an anhydride, and when heated more strongly it carbonizes with the dissemination of a characteristic odour and formation of pyroracemic and pyrotartaric acids. Oxidation converts it either into dioxy-tartaric or tartronic acid, and then into formic and carbonic acids, etc. It is employed in medicine, dyeing, etc.

Neutral potassium tartrate, $C_4H_4O_6K_2 + \frac{1}{2}H_2O$, forms monoclinic prisms easily soluble in water.

Acid potassium tartrate, **Tartar**, or Cremor tartari, $C_4H_5O_6K$. Small rhombic crystals of acid taste, sparingly soluble in water; is much used in dyeing, medicine, etc.

Potassium-sodium tartrate, **Rochelle** or **Seignette salt**, $C_4H_4O_6KNa + 4H_2O$ (1672), forms magnificent rhombic prisms.

Calcium tartrate, $C_4H_4O_6Ca + 4H_2O$, is a powder insoluble in water but soluble in cold caustic soda solution; on warming the solution it separates as a jelly, which redissolves upon cooling.

Potassio-antimonious tartrate, **Tartar emetic**, $C_4H_4(SbO)'KO_6 + \frac{1}{2}H_2O$ (see B. 15, 1540), is obtained by heating cream of tartar with antimony oxide and water. Rhombic efflorescent octahedra, easily soluble in water. It is poisonous and acts as an emetic, and is used as a mordant in dyeing.

Fehling's solution is a solution of cupric sulphate mixed with alkali and seignette salt.

The **Di-ethyl ether** is a thick oil, while the **Mono-ethyl ether** crystallizes

in prisms. **Aceto-tartaric acid** and **Amides** of tartaric acid are known, and also various anhydrides. As an alcohol, it forms with nitric acid a dinitric ether, the so-called **Nitro-tartaric acid**, $C_2H_2(O.NO_2)_2(CO_2H)_2$, which as an ether is readily saponifiable and, generally speaking, easily decomposable with formation of Dioxy-tartaric or of tartronic acid.

2. **Lævo-tartaric acid** is identical in its chemical and also in almost all its physical properties with ordinary tartaric acid, but differs from it in that it turns the plane of polarization of light to the left, in a degree equal to that in which the other turns it to the right. The crystallized salts show hemihedral faces like the salts of dextro-tartaric acid, but oppositely situated (see below). When equal quantities of both acids are mixed together in aqueous solution, the solution becomes warm, and we obtain:—

3. **Racemic acid**, $C_4H_6O_6 + H_2O$, the composition of which was first established by *Berzelius*, who recognized it as being different from tartaric acid, and who developed the idea of isomerism from this first example in 1829. Racemic acid is obtained from tartar mother liquor. It differs from dextro-tartaric acid in that its crystals are rhombic and efflorescent and also less soluble in water than the former; further, the free acid is capable of precipitating a solution of calcium chloride and is optically inactive (see below). The salts, which are termed racemates, and also the ethers (B. 21, 518), show small differences from the tartrates in the proportions of their water of crystallization and in solubility. In dilute aqueous solution **racemic acid** is completely split up into *d*- and *l*-tartaric acids.

When a solution of sodium-ammonium racemate, $C_4H_4Na(NH_4)O_6 + 4H_2O$, is evaporated, beautiful rhombic crystals which show hemihedral faces are obtained. *Pasteur* observed that these faces were not always similarly situated, but that certain crystals were dextro-hemihedral while others were lævo-hemihedral, so that one crystal formed the reflected image of the other. The lævo-hemihedral crystals are optically dextro-rotatory and *vice versa*. If now the two kinds of crystals be separated from one another mechanically and the free acid liberated from each, this will be found to consist, not of racemic acid, but in the one case of dextro- and in the other of lævo-tartaric acid.

An analogous decomposition of racemic acid is also possible by means of the cinchonine salts or by the addition of certain ferments (cf. p. 39).

4. **Meso-tartaric acid**, a fourth tartaric acid, is inactive like the foregoing, but not decomposable into the active acids, although it can be transformed into the latter (see p. 260). It crystallizes in efflorescent rectangular plates. The acid potassium salt is easily soluble in water.

E. Penta- and Hexatomic dibasic Acids.

Pentatomic: Trioxy-glutaric acid, $C_3H_3(OH)_3(CO_2H)_2$.

Hexatomic: Dioxy-tartaric acid, $C_2(OH)_4(CO_2H)_2$ (see Ketonic acids).

Saccharic acid, Mucic ", Iso-saccharic " } $C_4H_4(OH)_4(CO_2H)_2$.

Many of these acids form lactones (p. 233), the so-called lactonic acids, and some of them also double lactones (cf. *Fittig*, A. **255**, 1, *et seq.*).

Trioxy-glutaric acid, $CO_2H—(CH.OH)_3—CO_2H$, is a frequent oxidation-product of sugar-varieties, *e.g.* of xylose and arabinose. According to theory, four stereo-isomers may exist.

Saccharic acid, $C_4H_4(OH)_4(CO_2H)_2$, is produced by the oxidation of cane sugar, glucose, gulose, gulonic acid, mannite, or starch by nitric acid, and exists in the dextro-, lævo-, and inactive-forms (see Glucoses); *d*-saccharic acid passes into glycuronic acid upon reduction (see p. 240). All the three varieties are deliquescent.

Mucic acid, $C_4H_4(OH)_4(CO_2H)_2$, is formed by oxidizing dulcite, the gums, mucilages, and milk sugar. It is a sparingly soluble, colourless, crystalline powder. The molecule being symmetrical in structure, it is optically inactive. It is easily converted into derivatives of furfurane (p. 326).

Iso-saccharic acid, $C_6H_4(OH)_4(CO_2H)_2$, is obtained by the oxidation of glucosamine, $C_6H_{11}O_5(NH_2)$.

Theoretically ten stereo-isomeric acids of the formula, $C_6H_4(OH)_4(CO_2H)_2$, are possible, most of which (*e.g.* **d- and i-Manno-saccharic acids, Talo-mucic acid**, etc.) have been prepared by *E. Fischer* (B. **24**, 539, 2137, 3622). For their relations to the hexoses, see the table appended to these (p. 311).

F. Dibasic Ketonic Acids.

Dibasic ketonic acids unite in themselves the properties of a ketone and of a dibasic acid. The following are known:

1. **Mesoxalic acid**, $CO(CO_2H)_2$ or $C(OH)_2(CO_2H)_2$ (see p. 259), is prepared from dibromo-malonic acid, $CBr_2(CO_2H)_2$, and baryta water or oxide of silver, thus:

$$CBr_2(CO_2H)_2 + H_2O = CO(CO_2H)_2 + 2HBr;$$

also by boiling alloxan (p. 303) with baryta water. It crystallizes in deliquescent prisms ($+ H_2O$).

As a ketone it combines with $NaHSO_3$, reacts with hydroxylamine (p. 155), and is reduced by nascent hydrogen to the corresponding secondary alcohol-acid, tartronic acid:

$$CO(CO_2H)_2 + H_2 = CH(OH)(CO_2H)_2.$$

Since the acid and its salts still retain a molecule of water at temperatures above 100°, this may be chemically bound as in chloral hydrate, corresponding to the formula, $C(OH)_2(CO_2H)_2$, "di-oxy-malonic acid." In fact, two modifications of the ethyl ester are known, viz., $C(OH)_2(CO_2C_2H_5)_2$ and $CO(CO_2C_2H_5)_2$.

2. **Oxalo-acetic acid** (*Butanone di-acid*), $CO_2H—CH_2—CO—CO_2H$, is formed as ethyl ether by the action of sodium ethylate upon a mixture of oxalic and acetic ethers, and also by the action of concentrated sulphuric acid upon acetylene-dicarboxylic ether. It is a colourless oil, but the alcoholic solution gives an intense dark red with ferric chloride. Like aceto-acetic ether, it is of service for many syntheses (*W. Wislicenus*).

3. **Acetone-dicarboxylic acid** (*Pentanone di-acid*), $C_5H_6O_5 = CO{=}(CH_2—CO_2H)_2$, results upon treating citric acid with concentrated H_2SO_4. It breaks up readily into acetone and $2CO_2$ (see A. **261**, 151).

4. **Dioxy-tartaric acid**, $CO_2H — CO — CO — CO_2H$, or probably $CO_2H—C(OH)_2—C(OH)_2—CO_2H$, is formed from pyro-catechin and nitrous acid, and by the gradual decomposition of nitro-tartaric acid. It is crystalline. M. Pt. 98°. The characteristic difficultly soluble sodium salt decomposes easily into CO_2 and tartronate of sodium. It reacts with two mols. hydroxylamine. With phenyl-hydrazine-sulphonic acid, a yellow dye "tartrazine" is produced (cf. *Kekulé*, A. **221**, 230). Sodium bisulphite converts it into glyoxal.

5. **Acetone-diacetic acid**, *hydrochelidonic acid*, $CO(CH_2—CH_2—CO_2H)_2$. Cf. A. **253**, 206.

6. **Diaceto-succinic acid**, $\begin{array}{l}CH_3—CO.CH.CO_2H\\ \quad\quad\quad\quad |\\ CH_3—CO.CH.CO_2H\end{array}$ (see p. 246). The ester

of this is closely related to acetonyl-acetone, the latter being readily obtainable from the former by the action of caustic soda solution ("Ketonic decomposition;" cf. B. 22, 2100).

XI. TRI- TO HEXABASIC ACIDS.

The tribasic organic acids are those which, like phosphoric acid, are capable of forming three series of salts, viz., neutral, mono-acid, and di-acid salts. They contain according to theory three carboxyl groups. There are not only triatomic tribasic acids, such as methane- and propane-tri-carboxylic acids, etc., which are of purely acid character, but also tetratomic, pentatomic and hexatomic tribasic acids, alcoholic acids which possess at the same time the characters of alcohols. Further, these may be derived either from saturated or from unsaturated hydrocarbons.

A. Triatomic tribasic Acids.

1. Ethane-tricarboxylic acid, $C_2H_3(CO_2H)_3$,
2. Propane-tricarboxylic " $C_3H_5(CO_2H)_3$,
3. Tricarballylic " $C_3H_5(CO_2H)_3$.

The above acids 1 and 2 have been prepared by the malonic ether synthesis; they are best known as ethers, since, in the free state, they readily break up upon heating into CO_2 and dibasic acids.

Propane-tricarboxylic acid is unsymmetrically constituted.

Tricarballylic acid (*Pentane di-acid-3-carboxylic acid*), *symmetrical propane-tricarboxylic acid*, $C_3H_5(CO_2H)_3$. Occurs in unripe beet, and is prepared (*a*) by the addition of hydrogen to aconitic acid; (*b*) by heating citric acid with hydriodic; and (*c*) synthetically from glycerine by transforming it into tribromhydrin, $C_3H_5Br_3$, treating this with KCN, and saponifying the cyanide formed, $C_3H_5(CN)_3$. Since the three hydroxyls in glycerine are distributed among three carbon atoms, the same holds good for the carboxyls in the acid, which has therefore the symmetrical constitution;

$$\begin{array}{l} CH_2—CO_2H \\ \dot{C}H—CO_2H \\ \dot{C}H_2—CO_2H. \end{array}$$

This acid is of importance in determining the constitution of citric acid, from which, as already seen, it can be obtained by heating with HI. It crystallizes in rhombic prisms, easily soluble in water, etc. M. Pt. 166°.

For a synthesis of aconitic acid from acetic and oxalic acids (which perhaps approximates to the method of its formation in plants), see B. **24**, 120.

B. An Unsaturated tribasic Acid

is **Aconitic acid**, $C_6H_6O_6$, = $C_3H_3(CO_2H)_3$, which contains two atoms of hydrogen less than tricarballylic acid. It is found in nature, in Aconitum Napellus, shavegrass, sugar cane, beetroot, etc., etc., and is prepared by heating citric acid, $C_6H_8O_7$, water separating. It is a strong acid, crystallizable, and easily soluble in water. M. Pt. 191°. Nascent hydrogen transforms it into tricarballylic acid, hence it is an unsaturated acid and its constitution is:

$$\begin{array}{l} CH—CO_2H \\ \ddot{C}—CO_2H \\ \dot{C}H_2—CO_2H. \end{array}$$

C. Tetratomic tribasic Acids.

Citric acid, *acidum citricum*, $C_6H_8O_7$, = $C_3H_4(OH)(CO_2H)_3$. (*Scheele*, 1784; recognized as tribasic by *Liebig* in 1838.) Occurs in the free state in lemons, oranges and red bilberries, and mixed with malic acid in gooseberries, etc., also as calcium salt in wood, potatoes, beetroot, etc.

Preparation. From the juice of lemons by means of the lime salt.

Properties. Large rhombic prisms (+ H_2O), very easily soluble in water and rather easily in alcohol, but only slightly in ether. It loses its water of crystallization at 130°, melts

at 153°, and breaks up at a higher temperature first into aconitic acid and water, and then into carbon dioxide, itaconic acid, citraconic anhydride, and acetone. Oxidizing agents effect a very thorough decomposition.

Citrate of calcium is precipitated as a white sandy powder upon boiling a mixture of calcium chloride and alkaline citrate. The three series of salts are well characterized; the alkaline salts are soluble in water, the others mostly insoluble. Among the derivatives may be mentioned **mono-, di-,** and **tri-ethyl citrates** and **tri-ethyl aceto-citrate,** $C_3H_4(O.C_2H_3O)(CO_2C_2H_5)_3$, which last forms a proof of the alcoholic character of citric acid; it boils without decomposition. The **Amides** of citric acid are converted by concentrated H_2SO_4 into **Citrazinic acid,** $C_6H_5NO_4$, a pyridine derivative, (B. **17**, 2681.)

The *constitution* of citric acid is arrived at both from its relation to aconitic acid, which results from it as ethylene does from alcohol, and from various syntheses; it is:

$$\begin{array}{l} CH_2—CO_2H \\ \dot{C}(OH)—CO_2H \\ \dot{C}H_2—CO_2H. \end{array}$$

Thus it is obtained from β-dichloro-acetone as follows:

CH_2Cl	CH_2Cl	CH_2Cl	$CH_2.CN$	$CH_2.CO_2H$
$\dot{C}O$	$\dot{C}(OH)$-CN	$\dot{C}(OH)$-CO_2H	$\dot{C}(OH)$-CO_2H	$\dot{C}(OH).CO_2H$
$\dot{C}H_2Cl$	$\dot{C}H_2Cl$	$\dot{C}H_2Cl$	$\dot{C}H_2.CN$	$\dot{C}H_2.CO_2H.$

An **Iso-citric acid,** isomeric with citric, has also been prepared synthetically, (*Fittig*, B. **20**, 3179).

Appendix. D. Pentatomic tribasic acids. Desoxalic acid, $C_5H_6O_8$, = $C_2H(OH)_2(CO_2H)_3$, and **Oxy-citric acid,** $C_6H_8O_8$, the latter of which is present in the juice of turnips.

E. Tetra-, penta-, and hexabasic acids do not occur in nature but have been prepared in considerable numbers by means of the aceto-acetic or malonic ether synthesis, *e.g.*, ethane-tetra-carboxylic acid, propane-penta-carboxylic acid and butane-hexa-carboxylic acid. They are obtained in the form of ethers, most of them being either very unstable or incapable of existence in the free state. For their preparation, see B. **15**, 1109; **17**, 2781; A. **214**, 31. Acids up to a basicity of fourteen have now been synthetized (B. **21**, 2111).

XII. CYANOGEN COMPOUNDS.

Under the name of the cyanogen compounds is included a group of bodies which are derivable from cyanogen, C_2N_2. Cyanogen itself is a gas of excessively poisonous properties which behaves in many respects like a halogen, and its hydrogen compound, hydrocyanic acid, HCN, is an acid which is very similar in many ways to hydrochloric. In many cyanogen compounds the monovalent group (CN) plays the part of an element; cyanogen is to be regarded as the isolated radicle (CN), often written Cy, which however possesses the double formula C_2N_2, just as a molecule of chlorine (Cl_2) is made up of two atoms. The cyanogen group is further capable of combining with the halogens, hydroxyl, sulphydril (SH), amidogen, etc., etc. From the compounds so obtained numerous others are derived by the entrance of alcohol radicles in place of hydrogen. Such derivatives invariably exist in two isomeric forms, sharply distinguished from one another by their properties, and whose isomerism is of very great interest. (See table, pp. 270 and 271.)

There exist further polymeric modifications of most of those compounds (see table). The number of cyanogen compounds known is thus a very large one.

Formation. 1. Carbon and nitrogen cannot combine directly with one another but only when they are heated in presence of an alkali; thus, when nitrogen is led over a red-hot mixture of coal and carbonate of potash, potassium cyanide, KCN, is formed (this especially under a high pressure).

2. By passing ammonia over red-hot coal, ammonium cyanide, NH_4CN, is produced.

3. Carbon and nitrogen combine most readily with metals when in the nascent state, *e.g.*, when nitrogenous organic compounds such as leather, horn, claws, wool, blood, etc., are heated with potashes.

4. Hydrocyanic acid is formed when electric sparks are passed through a mixture of acetylene and nitrogen, and also by the action

[*Continued on p.* 272.

SUMMARY OF THE CYANOGEN COMPOUNDS AND

Relation to carbonic acid, etc. (See p. 290.)	Original Compounds.		
		Normal Form.	Isomeric Form.
Nitrile of oxalic acid,	*Cyanogen,*	C_2N_2	—
Nitrile of formic acid,	*Hydrocyanic acid,* Alcoholic derivatives : (*a*) Nitriles, (*b*) Iso-nitriles,	N≡C.H CH_3—C≡N —	— — CH_3—N
	Cyanogen chloride, bromide, iodide,	N≡C.Cl	—
$CO_3H_2+NH_3-2H_2O$, (Partial Nitrile, eventually Carbimide, see p. 290),	*Cyanic acid,* Alcoholic derivatives : (*a*) Methyl cyanate, (*b*) ,, iso-cyanate,	N≡C—OH N≡C—O.CH_3 —	— — O=C=N.
	Thiocyanic acid, Alcoholic derivatives : (*a*) Ethyl thiocyanate, (*b*) Allyl iso-thio-cyanate,	N≡C—SH N≡C—S.C_2H_5 —	— — S=C=N(
$CO_3H_2+2NH_3-3H_2O$, (Nitrile and amide, eventually Carbo-di-imide, see p. 290),	*Cyanamide,* Alkylated : (*a*) Alkyl cyanamide, (*b*) Carbo-di-imide,	N≡C—NH_2 N≡C—NH.CH_3 —	— — RN=C=
$CO_3H_2+NH_3-H_2O$, (Aminic acid),	*Carbamic acid,*	$CO(NH_2)OH$	—
$CO_3H_2+2NH_3-2H_2O$, (Carbamide),	*Urea,*	$CO(NH_2)_2$	—
	Thio-urea, Alkylated : (*a*) Alkyl-thio-ureas, (*b*) Imido-thio-carbamine compounds,	$CS(NH_2)_2$ CSN_2H_3R —	— — C(NH)$^{N}_{S}$
$CO_3H_2+3NH_3-3H_2O$, (Amidines),	*Guanidine,*	$C(NH)(NH_2)_2$	—

R = Alcohol radicle.

SEVERAL RELATED CARBONIC ACID DERIVATIVES.

POLYMERIC COMPOUNDS.

	Normal Form.	Isomeric Form.
Paracyanogen,	$(CN)_x$, perhaps $(C_3N_3)_2$	—
"*Tri-hydrocyanic acid,*"	$(CNH)_x$	—
Alcoholic derivatives:		
Tri-ethyl tri-cyanide,	$(CN)_3(C_2H_5)_3$	—
Cyanuric chloride, etc.,	$(CN)_3Cl_3$	—
Cyanuric acid,	$(CN)_3.(OH)_3$	—
Alcoholic derivatives :		
(*a*) Cyanurates,	$(CN)_3.(OC_2H_5)_3$	—
(*b*) Iso-cyanurates,	—	$(CO)_3.(NC_2H_5)_3$
Thio-cyanuric acid,	$(CN)_3.(SH)_3$	—
Alcoholic derivatives :		
(*a*) Thio-cyanurates,	$(CN)_3.(SC_2H_5)_3$	—
Dicyan-diamide,	$C_2N_4H_4$	—
Melamine,	$(CN)_3.(NH_2)_3$	—
Alkylated :		
(*a*) Alkyl-melamine,	$(CN)_3.(NHC_2H_5)_3$	—
(*b*) Alkyl-iso-melamine,	—	$(C:NH)_3(NC_2H_5)_3$
No Polymers.		

of the silent electric discharge on a mixture of cyanogen and hydrogen. For further modes of formation, see below.

The original material for the preparation of most of the cyanogen compounds is potassic ferrocyanide, which is manufactured on the large scale and possesses the great advantages over potassium cyanide of being stable in the air and non-poisonous.

A. Cyanogen and Hydrocyanic Acid.

Cyanogen, C_2N_2. Discovered by *Gay-Lussac* in 1815.

Occurs in the gases of blast-furnaces.

Formation. 1. As the nitrile of oxalic acid, by the abstraction of the elements of water from oxalate of ammonia by means of P_2O_5; also in the same way from the intermediate product of this reaction, oxamide:

$$C_2O_4(NH_4)_2 - 4H_2O = C_2N_2;$$
$$C_2O_2(NH_2)_2 - 2H_2O = C_2N_2.$$

2. By heating silver cyanide, AgCN, or mercuric cyanide, $Hg(CN)_2$, strongly; this is the method followed for its preparation:

$$Hg(CN)_2 = Hg + C_2N_2.$$

Further, in the wet way, by heating a solution of cupric sulphate with potassium cyanide, (B. **18**, Ref. 321).

Cyanogen is a colourless gas of a peculiar unpleasant odour resembling that of bitter almonds, and is terribly poisonous. Sp. Gr. 1·8. Easily condensible. M. Pt. $-34°$. B. Pt. of liquid cyanogen $-21°$. Soluble in $\frac{1}{4}$ vol. of water and in even less alcohol. The solutions become dark upon standing, with separation of a brown powder ("Azulmic acid"), while oxalic acid, ammonia, formic acid, hydrocyanic acid and urea are to be found in the liquid.

The formation of the oxalic acid and ammonia depends upon normal saponification, and that of formic acid upon the saponification of the

hydrocyanic acid formed as an intermediate product. In presence of a minute quantity of aldehyde, oxamide results from the taking up of water. Cyanogen combines with heated potassium to KCN, and dissolves in aqueous potash to form KCN and KCNO. It yields with H_2S the thiamides **Flavean hydride**, $NC—CS.NH_2$, and **Rubean hydride**, $CS(NH_2)—CS(NH_2)$.

Paracyanogen $(CN)_x$ is a polymer of cyanogen. It is an amorphous brown powder which results as a bye-product when mercuric cyanide is heated; upon further heating, it is transformed into cyanogen.

Hydrocyanic acid, *prussic acid*, CNH. Discovered about the year 1782 by *Scheele*, and investigated closely by *Gay-Lussac*.

Formation. 1. By decomposing metallic cyanides by means of stronger acids; also by the distillation of potassic ferrocyanide with dilute sulphuric acid:

$$K_4Fe(CN)_6 + 5H_2SO_4 = 6HCN + FeSO_4 + 4KHSO_4.$$

The ferrous sulphate produced reacts with more ferrocyanide to form ferro-potassic ferrocyanide, $FeK_2(FeCy_6)$ (see p. 277), which is not affected by dilute acids; consequently only half of the cyanogen present is converted into hydrocyanic acid. When concentrated instead of dilute sulphuric acid is employed, carbonic oxide and not hydrocyanic acid is obtained.

2. From ammonium formate or formamide by the separation of water:

$$H.CO.O(NH_4) = H.CO.NH_2 + H_2O = HCN + 2H_2O.$$

Hydrocyanic is therefore the nitrile of formic acid.

3. Together with oil of bitter almonds, C_7H_6O, and grape sugar, $C_6H_{12}O_6$, through the decomposition of amygdalin under the influence of "emulsin," (see p. 322):

$$C_{20}H_{27}NO_{11} + 2H_2O = CNH + C_7H_6O + 2C_6H_{12}O_6.$$

The oil of bitter almonds and its aqueous solution—(aqua amarum amygdalarum)—prepared from the almonds themselves, consequently contain HCN.

4. By the action of ammonia upon chloroform under pressure:

$$CHCl_3 + NH_3 = HCN + 3HCl.$$

5. Through the oxidation of many organic substances by means of nitric

Preparation. From yellow prussiate of potash. In order to obtain the anhydrous acid, the vapours are dried over calcium chloride.

Properties. Colourless liquid, solidifying at $-15°$. Sp. Gr. 0·70. B. Pt. 26·5°. It has a peculiar odour and produces an unpleasant irritation in the throat, is miscible with water, etc., and burns with a violet flame. Like potassium cyanide, it is one of the most terrible of poisons. When absolutely pure it can be preserved unchanged, but it decomposes in presence of traces of water or ammonia, with separation of a brown mass and formation of ammonia, formic acid, oxalic acid, etc. The addition of minute quantities of mineral acids renders the aqueous solution more stable.

Hydrocyanic acid combines with nascent hydrogen to methylamine:

$$HCN + 2H_2 = HCH_2.NH_2.$$

With hydrochloric acid it forms a white crystalline product ($HCN + HCl$), which appears to be the imido-chloride of formic acid, $H-CCl=NH$. It also combines with many metallic chlorides to crystalline compounds which are easily decomposable.

Hydrocyanic acid is a weak monobasic acid, in accordance with the mildly acidifying nature of the cyanogen radicle; its salts are decomposed even by carbonic acid. Its *constitutional formula*, $H-C\equiv N$, follows from its relations to formic acid and chloroform. In some reactions, however, it yields compounds which are derived from its hypothetical isomer $=C=N-H$ or $C\equiv N-H$. Its alcoholic derivatives each exist in two isomeric modifications, nitriles and iso-nitriles, which are derived from the two atomic groups $H-CN$ and $CN-H$. (See table, p. 270, and the appendix to the cyanogen group, p. 286.)

Hydrocyanic acid can be detected by converting it either into Prussian blue or into ferric sulphocyanide. In the former case the solution to be tested is treated with excess of caustic soda and some ferrous and ferric salt, boiled, and acidified, when Prussian blue results; in the latter the solution is evaporated to dryness along with a little yellow sulphide of ammonium, the residue taken up with water and ferric chloride added, when the blood-red colour of ferric sulphocyanide is obtained.

Tri-hydrocyanic acid, $(CNH)_x$, results from the polymerization of hydrocyanic acid under certain specified conditions. It forms white acute-angled crystals which go back into hydrocyanic acid with violence when heated above 180°. Its molecular weight is still unknown.

Potassium cyanide, KCN. For *formation*, see p. 269.

Preparation. 1. Anhydrous ferrocyanide of potassium is heated to fusion:

$$K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2.$$

In order to prevent the decomposition of a portion of the cyanide, potash may be added to the melted mass, but the product will in this case contain potassic cyanate, (*Liebig's* cyanide of potash.)

2. By heating potassium in cyanogen gas.

3. By the combination of HCN with KOH, and precipitation from the aqueous solution by means of alcohol.

Properties. Colourless deliquescent cubes, readily soluble in water but only slightly in alcohol. It is sold in sticks. It absorbs water from the air and is decomposed by the carbonic acid of the latter. The aqueous solution precipitates nearly all the metallic salts, the precipitates redissolving in excess, with formation of double cyanides.

Simple Cyanides.

Ammonium cyanide, $NH_4.CN$. White deliquescent mass. It is also produced by the passage of the silent electric discharge through a mixture of marsh gas and nitrogen.

Mercuric cyanide, $Hg(CN)_2$. Colourless prisms, stable in the air and readily soluble in water. Excessively poisonous.

Silver cyanide, AgCN. White flocculent precipitate, closely resembling chloride of silver both in appearance and solubility.

Double Cyanides.

The double cyanides, which are produced by dissolving the insoluble metallic cyanides in a solution of cyanide of potassium, are divided into two classes. The members of the one class are broken up again on the addition of dilute mineral

acids, with separation of the insoluble cyanide and formation of hydrocyanic acid, *e.g.* KCN + AgCN; 2KCN + $Ni(CN)_2$. The members of the other class do not separate hydrocyanic acid, but comport themselves as salts of particular acids; to the latter belong, in especial, potassic ferrocyanide, K_4FeCy_6, (= 4KCy + $FeCy_2$), and potassic ferricyanide, K_3FeCy_6, (= 3KCy + $FeCy_3$),* which yield with acids hydro-ferro- and hydro-ferricyanic acids. Many salts of the latter acid are not decomposed at all by dilute acids, for instance Prussian blue, but they are by caustic potash (which converts Prussian blue into $Fe(OH)_3$ and K_4FeCy_6).

Potassium ferrocyanide, *yellow prussiate of potash*, $K_4FeCy_6 + 3H_2O$. *Formation.* 1. By adding excess of potassium cyanide to a solution of ferrous sulphate.

2. By dissolving iron in a solution of cyanide of potassium, when hydrogen is evolved, thus:

$$2KCN + Fe + 2H_2O = Fe(CN)_2 + 2KOH + H_2;$$
$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Iron is therefore previously added to the "melt" in practical working (see p. 269, 3).

It forms large lemon-coloured tetragonal plates, which are stable in the air and easily soluble in water, but insoluble in alcohol. Concentrated HCl separates **Hydro-ferrocyanic acid,** H_4FeCy_6, in white decomposable needles. With a solution of $CuSO_4$, a red-brown precipitate of **Cupric ferrocyanide,** or *Hatchett's* brown, Cu_2FeCy_6, is thrown down, and with solutions of ferrous and ferric salts the well known characteristic precipitates. Chlorine oxidizes it to

Potassium ferricyanide, *red prussiate of potash*, K_3FeCy_6, thus:

$$2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl.$$

This crystallizes in long dark-red monoclinic prisms which are readily soluble in water. The solution decomposes upon standing, and acts as a strong oxidizing agent in the presence of alkali, K_4FeCy_6 being reproduced.

* For the sake of brevity, iron is here and in the following pages [illegible] as di- and trivalent.

Hydro-ferricyanic acid, H_3FeCy_6, forms brown needles, and is easily decomposed.

FERRO- AND FERRI-CYANIDES OF IRON.

	Ferrocyanides.	Ferricyanides.
Ferrous salts,	Potassium-ferro-ferrocyanide, $K_2Fe^{II}(FeCy_6)^{IV}$, from $FeSO_4$ + K_4FeCy_6; white, becoming rapidly blue in the air from conversion into	*Turnbull's* blue, $Fe_3^{II}(FeCy_6)_2^{III}$, from $FeSO_4$ + K_3FeCy_6.
Ferric salts,	Potassium-ferri-ferrocyanide, $KFe^{III}(FeCy_6)$.	($FeCl_3 + K_3FeCy_6$ give no precipitate, but only a brown colouration.)
	Insoluble Prussian blue or *Williamson's* blue, $Fe_4^{III}(FeCy_6)_3$, from $FeCl_3$ + K_4FeCy_6; blue powder with a copper glance.	
	$KFe^{III}(FeCy_6)^{IV}$ = Soluble Prussian blue, from ferric or ferrous salts and excess of ferro- or ferri-cyanide of potassium.	$KFe^{II}(FeCy_6)^{III}$ =

The formation of Prussian blue was first observed by *Diesbach* soon after the year 1700.

As regards the *constitution* of hydro-ferro- and hydro-ferricyanic acids, one may make the assumption that they contain the trivalent radicle $(C_3N_3)^{III}$, "tricyanogen," of cyanuric acid (see p. 280):

$$\begin{matrix}K_2=(C_3N_3)\\K_2=(C_3N_3)\end{matrix}>Fe^{II} \qquad \begin{matrix}K-(C_3N_3)\\K_2=(C_3N_3)\end{matrix}>Fe^{III}$$

Potassium ferrocyanide. Potassium ferricyanide.

$$Fe^{III}<\begin{matrix}(C_3N_3)—Fe^{II}—(C_3N_3)\\(C_3N_3)=Fe^{II}\quad Fe^{II}=(C_3N_3)\end{matrix}>Fe^{III}, \text{ and so on.}$$

Turnbull's blue.

When ferrocyanide of potassium is oxidized by nitric acid, there is formed **Nitro-prussic acid,** whose sodium salt, $FeCy_5(NO)Na_2 + 2H_2O$, crystallizes in red prisms soluble in water and forms a valuable reagent for the detection of sulphuretted hydrogen, an alkaline solution yielding with the latter a splendid but transient purple-blue colouration.

B. Halogen Compounds of Cyanogen.

Cyanogen chloride, CN.Cl, (*Berthollet*). Colourless condensible gas of a most obnoxious pungent odour, somewhat soluble in water. B. Pt. of its liquid 15·5°. It is prepared by the action of chlorine upon mercuric cyanide or upon dilute aqueous hydrocyanic acid, thus :

$$CNH + Cl_2 = CNCl + HCl.$$

It polymerizes readily to cyanuric chloride, and yields potassic chloride and cyanate with aqueous potash, appearing thus as the chloride of cyanic acid :

$$CN.Cl + 2KOH = CN.OK + ClK + H_2O.$$

Cyanogen bromide, CNBr. Analogous to the chloride. Transparent prisms.

Cyanogen iodide, CNI. Beautiful white prisms, smelling intensely both of cyanogen and iodine, and subliming with the utmost ease. Very poisonous. Prepared from mercuric cyanide and iodine.

Cyanuric chloride, *tri-chloro-cyanogen,* $(CN)_3Cl_3$. This polymer is obtained from cyanogen chloride, or from hydrocyanic acid and chlorine in ethereal solution. It forms beautiful white crystals, of an unpleasant pungent odour. M. Pt. 145°, B. Pt. 190°. Boiling water decomposes it with formation of hydrochloric acid and cyanuric acid, $(CN)_3.(OH)_3$, of which latter it appears as the chloride. It contains the trivalent radicle $(CN)_3{}^{'''}$ = tri-cyanogen, (see Cyanuric acid).

C. Cyanic and Cyanuric acids.

Cyanuric acid is formed when urea is heated, either alone or in a stream of chlorine gas ; by subjecting it to dry distillation and condensing the vapours evolved in a freezing mixture, one obtains **Cyanic acid,** CNOH, as a mobile liquid of a pungent odour :

$$C_3N_3O_3H_3 = 3CNOH.$$

It is exceedingly unstable ; when taken out of the freezing mixture it changes, with explosive ebullition, into the poly-

meric **Cyamelide**, $(CONH)_x$, a white porcelain like mass which goes into cyanic acid again upon heating. Cyanic acid combines with ammonia to cyanate of ammonium.

Potassium cyanate, CNOK, frequently also termed potassium isocyanate, is prepared by the oxidation of an aqueous solution of potassic cyanide by means of permanganate (A. 259, 377); or by fusing potassic cyanide or yellow prussiate of potash with PbO_2 or MnO_2: (CNK + O = CNOK). White plates, readily soluble in water and alcohol. It yields hydrazo-dicarboxylic amide (p. 299) with hydrazine sulphate (A. 271, 127).

Ammonium cyanate, $CNO(NH_4)$, forms a white crystalline mass, and is of especial interest on account of the readiness with which it changes into the isomeric urea, CON_2H_4.

When hydrochloric acid is added to these salts, there result —instead of free cyanic acid—its products of saponification, CO_2 and NH_3:— $CONH + H_2O = CO_2 + NH_3$.
This decomposition is avoided by the addition of dilute acetic acid (instead of hydrochloric), but in the latter case the cyanic acid changes into its polymer cyanuric acid, the hydrogen-potassium salt of the latter slowly crystallizing out.

From cyanic acid are derived two isomeric classes of alcoholic derivatives, by the replacement of the hydrogen by alcohol radicles. The derivatives which are constituted on the type N≡C.OR are termed the *normal*, and those on the type O=C=NR the *iso-compounds*.

I. When potassium cyanate is distilled with ethyl iodide or, better, with potassium ethyl-sulphate, there is obtained

Ethyl iso-cyanate or *cyanic ether*, $CO.NC_2H_5$, a colourless liquid of suffocating odour, which boils unchanged at 60° and is decomposed by water. It does not possess the properties of a compound ether, but is broken up by alkalies or acids into ethylamine and carbon dioxide, thus:

$$CONC_2H_5 + H_2O = CO_2 + NH_2.C_2H_5.$$

Water, which acts in a similar manner, gives rise to the more complicated urea derivatives; ammonia and amine bases

also produce derivatives of urea (p. 292), and alcohol yields derivatives of carbamic acid (p. 291).

Constitution.—The formation of ethylamine proves that the N of the cyanic ether is linked directly to the alcohol radicle, so that the constitution is: $O{=}C{=}N.C_2H_5$. It is questionable, however, whether free cyanic acid and cyanate of potassium possess analogous constitutions, since frequent observations have shown that the normal cyanic compounds readily change into the iso-(see below); theoretical considerations indeed make it more probable that cyanic acid has the constitution $N{\equiv}C{-}OH$, according to which it appears as the normal acid, with cyanogen chloride as its chloride. Potassium cyanate would then be $N{\equiv}C{-}O{-}K$.

Normal cyanic ethers are not known with certainty: cyan-etholine, $CN.OC_2H_5$, obtained by the action of cyanogen chloride upon sodium alcoholate, is looked upon as one of them.

Cyanuric acid, $C_3N_3O_3H_3$, $= (CN)_3(OH)_3$ (*Scheele*). The formation of cyanuric acid by heating urea, already mentioned on p. 278, is easily understood when one remembers that it is made up of the constituents of cyanic acid and ammonia, so that, when the latter is split off, the former becomes free and then polymerizes. Cyanuric acid forms transparent prisms which contain 2 mols. H_2O of crystallization and weather in the air, and which are readily soluble in hot water. It is a tribasic acid. The sodium salt is sparingly soluble in conc. NaOH; the $(Cu\text{-}NH_4)$ salt possesses a characteristic beautiful violet colour. Upon prolonged boiling with hydrochloric acid it is saponified to CO_2 and NH_3, while phosphorus pentachloride converts it into cyanuric chloride, the acid being regenerated from this by water.

Cyanuric acid also gives rise to two isomeric classes of alcoholic derivatives, viz.:

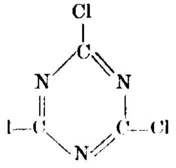
1. The **Normal cyanuric ethers**, *e.g.* $C_3N_3(OC_2H_5)_3$ (a colourless liquid), which result from the polymerization of the cyan-etholines and also by the action of methyl iodide etc. upon cyanurate of silver at the ordinary temperature. They easily change into the isomeric

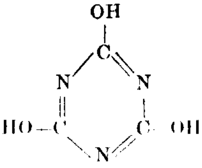
2. **Iso-cyanuric ethers** or *tri-carbimido ethers*, *e.g.* $C_3O_3(NC_2H_5)_3$, colourless liquids which frequently result instead of the cyanic ethers,

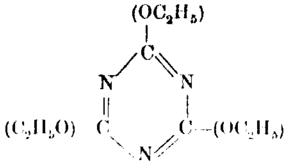
for example, on the distillation of cyanurate with ethyl-sulphate of potassium. They are further formed by the polymerization of the iso-cyanic ethers, being thus obtained as bye-products in the preparation of the latter.

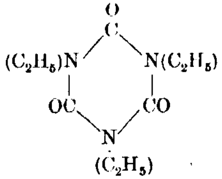
The normal compounds are broken up by saponification with the formation of alcohol, and the isomers with formation of ethylamine.

The *constitution* of cyanuric acid follows from its relation to cyanuric chloride as $(CN)_3(OH)_3$, and that of the alkyl derivatives from their behaviour upon saponification. The normal compounds therefore contain, like cyanuric chloride, the trivalent radicle tri-cyanogen, $(CN)_3$, whose N- and C-atoms one assumes to be linked to each other alternately by single and double bonds in a "closed ring," while the iso-cyanic ethers are to be regarded as derived from a hypothetical original substance consisting of three CO- and NH-groups joined together in the form of a ring (cf. *A. W. Hofmann*, B. **18**, 2755; *Ponomarew*, B. **18**, 3261; also Benzene derivatives):


Cyanuric chloride.


Cyanuric acid.


Cyanuric ether.


Isocyanuric ether.

In addition to cyanuric acid and cyamelide, various other polymers of cyanic acid have been described, but only some of them have been closely studied. (Cf. among others, J. pr. Ch. **32**, 461.)

Further, in the aromatic series, derivatives of a **Di-isocyanic acid**, $(CO)_2.(NH)_2$, are known, (B. **18**, 764).

D. Thiocyanic Acid and its Derivatives.

Potassium thiocyanate, *-sulphocyanate*, *-sulphocyanide*, *-rhodanide*, CNSK. Potassium cyanide not only combines readily with oxygen to cyanate but also with sulphur to thiocyanate, either when fused with sulphur or when its solution is evaporated with yellow sulphide of ammonium:

$$KCN + S = CNSK.$$

It is prepared by fusing yellow prussiate of potash with sulphur and potashes. It forms long colourless deliquescent prisms, extremely soluble in water with absorption of much heat, and also easily soluble in hot alcohol.

Ammonium thiocyanate, *ammonium rhodanide*, $CNS(NH_4)$, results upon warming a mixture of carbon bisulphide, concentrated ammonia and alcohol (*Millon*), di-thiocarbamate and tri-thiocarbonate of ammonia being formed as intermediate products (see p. 296):

$$CS_2 + NH_3 = CNSH + H_2S.$$

Colourless deliquescent plates, readily soluble in alcohol. Upon being heated to 130°–140°, it is partially transformed into the isomeric thio-urea, just as ammonium cyanate is into ordinary urea. It precipitates silver thiocyanate, CNSAg, (white) from solutions of silver salts, and is therefore employed in the titration of silver, with ferric sulphate as indicator; and it gives with ferric salts a dark blood-red colouration of **Potassium-ferri-thiocyanate**, $2\,Fe(CNS)_3 + 9KCNS + 4\,H_2O$. This last reaction is exceedingly delicate.

Mercurous thiocyanate, $Hg_2(CNS)_2$, is a white powder insoluble in water, which increases enormously in volume upon being burnt, (Pharaoh's serpents). The **Aluminium salt** is used in printing with alizarin red. The free **Thiocyanic acid**, CNSH, is obtained by decomposing its mercury salt with hydrochloric acid. It is a pale yellow liquid of pungent odour, and is only stable in a freezing mixture, or when in dilute aqueous solution. At the ordinary temperature it polymerizes to a yellow amorphous substance, and decomposes in concentrated aqueous solution, with formation of **Persulphocyanic acid**, $C_2N_2S_3H_2$ (yellow crystals).

Concentrated sulphuric acid decomposes the thiocyanates with formation of carbon oxy-sulphide: $CNSH + H_2O = COS + NH_3$; sulphuretted hydrogen decomposes them into carbon bisulphide and ammonia: $CNSH + H_2S = CS_2 + NH_3$.

Cyanogen sulphide, $(CN)_2S$, is to be regarded as the thio-anhydride of thiocyanic acid; it is prepared from cyanogen iodide and silver thiocyanate, and forms readily soluble plates of sharp odour.

Just as in the case of cyanic acid, so are there derived from thiocyanic acid two isomeric classes of alcoholic derivatives, by the replacement of hydrogen by alcohol radicles.

I. Compound ethers of thiocyanic acid result from the entrance of alcoholic radicles in the place of the hydrogen of the acid.

Ethyl thiocyanate, $CN.SC_2H_5$, is obtained either (1) by the distillation of potassium ethyl-sulphate with potassium thiocyanate, or (2) by the action of cyanogen chloride upon a mercaptide. It is a colourless liquid with a peculiar pungent odour of leeks, and almost insoluble in water. B. Pt. 142°. Alcoholic potash saponifies it in the normal manner with reproduction of potassium thiocyanate; in other reactions, however, the alcoholic radicle remains united to the sulphur.

Thus nascent hydrogen reduces it to mercaptan, and fuming nitric acid oxidizes it to ethyl-sulphonic acid.

It follows from mode of formation (2) and also from the reactions of the thiocyanic ethers that the sulphur in them is linked to the alcohol radicle. Consequently in the salts it is linked to the metal in question, and in the free acid to hydrogen. We have therefore the following *constitutional* formulae:

$N\equiv C—SH$	$N\equiv C—SK$	$N\equiv C—SC_2H_5$
Thiocyanic acid.	Potassium thiocyanate.	Ethyl thiocyanate.

Allyl thiocyanate, $CN.SC_3H_5$. Colourless liquid smelling of leeks. B. Pt. 161°. Changes upon distillation into the isomeric mustard oil.

II. Isomeric with the thiocyanic ethers are the mustard oils ("Senföle.")

Allyl iso-thiocyanate, common *mustard oil*, $CS:N.C_3H_5$, is

prepared by distilling the seeds of black mustard (Sinapis niger) with water. It is a liquid sparingly soluble in water and of exceedingly pungent odour, which produces blisters on the skin. B. Pt. 151°. It results on distilling allyl thiocyanate, by a molecular rearrangement, and it is also obtained by the action of carbon bisulphide upon the corresponding primary amine, allylamine, thus:

$$CS_2 + NH_2.C_3H_5 = CS:N.C_3H_5 + H_2S.$$

This reaction does not, however, proceed exactly as indicated in the above equation, there being first formed the allylamine salt of allyl-di-thiocarbamic acid, which is changed into allyl iso-thiocyanate upon distillation with mercuric chloride. (See di-thiocarbamic acid, p. 297.)

Ethyl iso-thiocyanate, $C_2H_5N.CS$, (B. Pt. 134°), and **Methyl iso-thiocyanate**, $CH_3N.CS$, (solid, M. Pt. 34°, B. Pt. 119°), etc., closely resemble the allyl compound, and are obtained in an analogous manner by the action of carbon bisulphide upon ethylamine, methylamine, etc.

The mustard oils also result from the distillation of alkylated thio-ureas (p. 298) with syrupy phosphoric acid (*Hofmann*, B. **15**, 985), or with concentrated hydrochloric acid. They break up on being saponified, with reproduction of the primary amines from which they can be prepared:

$$CS.NC_3H_5 + 2H_2O = NH_2.C_3H_5 + H_2S + CO_2.$$

They are connected with the thio-ureas by various reactions, and also with the cyanic ethers, since in the latter O can be replaced by S, but in the mustard oils, on the contrary, S by O.

The *constitution* of the mustard oils follows from their relation to the *primary amines, the alkyl being linked to nitrogen in both classes of* compounds; the *constitutional formula of methyl iso-thiocyanate* is therefore $S=C=N-CH_3$. Iso-thiocyanic acid, $SC=NH$, is itself unknown.

Polymers. **Dithio-dicyanic acid**, $C_2N_2S_2H_2$. The potassium salt of this polymer has been described, but little is known about it.

Thio-cyanuric acid, $(C_3N_3)(SH)_3$, is a tribasic acid. Yellow powder. The primary sodium salt, $C_3N_3(SH)_2SNa$, crystallizes well. It is formed *e.g.* by the action of cyanuric chloride upon sodium sulphide, whence its constitution follows. Its **Tri-methyl ether** results along with methyl iso-thiocyanate upon heating methyl thiocyanate to 180°; by the polymerization and subsequent molecular transformation of the latter (*A. W. Hofmann*, B. **18**, 2196; *Klason*, B. **19**, Ref. 136).

Polymeric mustard oils are also known (*Hofmann*, B. **25**, 876).

E. Cyanamide and its Derivatives.

Cyanamide, $CN.NH_2$, (*Bineau*), is formed :

1. By leading cyanogen chloride into an ethereal solution of ammonia :

$$CNCl + 2NH_3 = CN.NH_2 + NH_4Cl.$$

2. By the action of HgO upon thio-urea in aqueous solution, ("desulphurization") :

$$NH_2—CS—NH_2 = NC.NH_2 + H_2S.$$

Colourless crystalline hygroscopic mass, readily soluble in water, alcohol and ether. M. Pt. 40°. When heated to 150°, it changes into the polymeric dicyan-diamide with explosive ebullition; also on evaporating its solution or allowing it to stand. Dilute acids cause it to take up the elements of water, with formation of urea: $CN.NH_2 + H_2O = CON_2H_4$; and it combines *in an analogous manner with sulphuretted hydrogen* to thio-urea. When heated with ammonia salts it yields salts of guanidine.

Cyanamide behaves as a weak base, forming crystalline easily decomposable salts with acids and, at the same time, as a weak acid, yielding a sodium salt, CN.NHNa, a lead and a silver salt, etc. The last is a yellow powder and has the composition CN_2Ag_2.

Cyanamide also gives rise to two isomeric series of alcoholic derivatives, by the replacement of the hydrogen by alkyl.

I. **Methyl- and Ethyl-cyanamides** are prepared *e.g.* from methyl- and ethyl-thio-urea. **Di-ethyl-cyanamide**, $CN_2(C_2H_5)_2$, is obtained by treating silver-cyanamide with ethyl iodide. Acids saponify it to CO_2, NH_3 and $NH(C_2H_5)_2$, hence it possesses the constitution $N{\equiv}C—N(C_2H_5)_2$:

$$N{\equiv}C—N(C_2H_5)_2 + 2H_2O = NH_3 + CO_2 + NH(C_2H_5)_2.$$

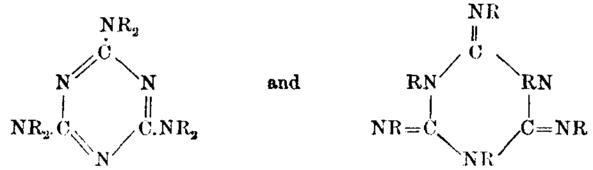
From this it follows that cyanamide has most probably the constitution which corresponds with its name, viz., $N{\equiv}C—NH_2$.

II. Other cyanamide derivatives, which are chiefly known in the aromatic series, spring from a hypothetical isomer of cyanamide, viz., **Carbo-di-imide**, $NH{=}C{=}NH$; for instance, **Diphenyl-carbo-di-imide**, $CN_2(C_6H_5)_2$. Boiling with acids likewise decomposes them into CO_2 and an amine, but the latter can only be a primary one.

Polymers. **Dicyan-diamide,** *parame,* $C_2N_4H_4$ (p. 285). Crystallizes in beautiful broad needles or prisms, and has probably the constitution $N{\equiv}C{-}NH{-}C{<}^{NH}_{NH_2}$ (B. **24**, 899). Like cyanamide, it yields melam when strongly heated.

Melamine, *cyanuramide,* $C_3N_6H_6$ (*Liebig,* 1838), forms glancing rhombic octahedra, insoluble in alcohol and ether, and possesses basic properties. When it is boiled with acids, the NH_2- groups are successively replaced by OH with the formation of **Ammeline,** $(CN)_3(NH_2)_2OH$, **Ammelide,** $(CN)_3NH_2(OH)_2$, and finally cyanuric acid, $(CN)_3(OH)_3$. Melamine has therefore the constitution $(CN)_3(NH_2)_3$, = tricyan-triamide.

Further, alkylated melamines are derived from melamine by the replacement of hydrogen by alkyl, and in addition to these there exists an isomeric class of compounds of which the hypothetical "Iso-melamine," $[C(NH)]_3(NH)_3$, is the basis. To this class belong the polymerization products of the alkyl cyanamides. The following constitutional formulae are ascribed to these two series (R = Alcohol radicle):



Melamines. and Iso-melamines.

For particulars see *A. W. Hofmann,* B. **18**, 2755, 3217; *Rathke,* B. **20**, 1056.

Melam, $[(CN)_3(NH_2)_2]_2NH$, is an imide of melamine, into which it is converted by ammonia (*Rathke, Smolka*), and by sulphuric acid. It forms a white powder, insoluble in water. It is prepared by heating cyanamide, dicyan-diamide, or ammonium thiocyanate strongly.

F. Appendix. Theoretical Considerations as to isomerism in the Cyanogen Group.

As has already been explained, there are derived from hydrocyanic acid, cyanic acid, thiocyanic acid and cyanamide, and also from their polymers, two classes of isomeric alcoholic derivatives which differ sharply from one another in their products of decomposition. They correspond, properly speaking, to two isomeric mother substances—the "normal" and "pseudo" forms (*Ad. Baeyer*)—only one of which, however, is known in the free state, viz., the normal compound (cf. *Hofmann,* loc. cit.; *Klason,* B. **20**, Ref. 317). The fact that the isomeric form has never been obtained may be explained by assuming that it represents an unstable state of equilibrium of the atoms and that when attempts are made to

prepare it, it immediately undergoes molecular transformation into the other, stable, form. When the hydrogen is replaced by alkyl, both varieties of atomic groups are in most cases capable of existence, although even here also a difference in stability is observed, the normal compounds changing very readily into the iso- (or pseudo-) compounds. In consequence of this one obtains the iso-cyanic ether directly from potassium cyanate instead of the normal one, allyl thiocyanate readily changes into the iso-thiocyanate, and iso-cyanuric ether is usually got instead of cyanuric, etc., etc. It is also conceivable that the mother substances may possess both the above constitutional formulae, *i.e.* that, by the wandering of an atom of hydrogen, their atoms may sometimes arrange themselves in the one and sometimes in the other form, and that they may accordingly show the reactions of either ("Tautomerism;" see p. 26; *Butlerow*, A. **189**, 76; cf. *Laar*, B. **18**, 648; **19**, 730; *Bamberger*, B. **23**, 1856). Among other compounds, regarding which considerations of this nature have been advanced, may be specially mentioned thio-urea, $CS(NH_2)_2$ or $C(NH)\begin{cases}NH_2\\SH\end{cases}$ (p. 297), amides of monobasic acids (see p. 197) and their thiamides, $R—CS.NH_2$ or $R—C\begin{matrix}\nearrow NH\\ \searrow SH\end{matrix}$ (p. 199), sodio-aceto-acetic ether (p. 245), diazo-benzene, phloroglucin, isatin, carbostyril, etc. One of the formulae in question of these substances is convertible into the other simply by the wandering of a hydrogen atom:—"hydrogen-isomerism." It has been proved that many of these compounds react in a manner which corresponds as well with the one formula as with the other. When a "change in the bonds" of such "tautomeric" substances occurs, it is termed "desmotropism" (*Hantzsch* and *Herrmann*, B. **20**, 2081; **21**, 1754; *Baeyer*, A. **245**, 189; *Förster*, B. **21**, 1857), or "iso-dynamic molecular transformation" (*Armstrong*). There can be no desmotropism when there is no longer present in the molecule a hydrogen atom capable of "wandering" (cf. B. 23, 1856).

XIII. CARBONIC ACID DERIVATIVES.

Carbonic acid is a dibasic acid, forming two series of salts, *e.g.* Na_2CO_3 and $NaHCO_3$. The hydrated acid itself, CO_3H_2, $= O{=}C\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$, is unknown, but may be supposed to exist in the aqueous solution.

Its empirical formula shows carbonic to be the lowest oxy-acid $C_nH_{2n}O_3$, *i.e.* it is homologous with glycollic acid and may be looked upon

as oxy-formic acid. Its dibasic nature is explained by the carbonyl group apparently extending its acidifying character over both hydroxyls equally. Since the latter are both linked to one carbon atom, the non-existence of the free hydrate is readily understood (see p. 142, etc.).

The salts of carbonic acid and those of several of its derivatives, such as carbon bisulphide, CS_2, and carbon oxy-sulphide, COS, have been already treated of under inorganic chemistry. But there still remain for description the compound ethers, chlorides and amides of carbonic acid, two series of which exist, acid and neutral, as in the case of all the dibasic acids, $C_nH_{2n-2}O_4$. The neutral compounds are well characterized and are very similar to those of oxalic or succinic acid; the acid compounds on the other hand are unstable in the highest degree when in the free state, and are known almost only as salts. Many mixed derivatives have also been prepared, *e.g.* carbamic ether, $CO(NH_2)(OC_2H_5)$, analogous to oxamethane (p. 252).

Summary.

Neutral derivatives.	$CO(OC_2H_5)_2$ Ethyl carbonate.	$COCl_2$ Carbonyl chloride.	$CO(NH_2)_2$ Urea.
Acid derivatives.	$CO(OC_2H_5).OH$ Ethyl carbonic acid.	$CO(Cl)(OH)$ Chloro-carbonic acid.	$CO(NH_2)(OH)$ Carbamic acid.
Mixed derivatives.		$CO(Cl)(OC_2H_5)$ Chloro-carbonic ether.	$CO(NH_2)(OC_2H_5)$ Urethane.

The *modes of formation* of these compounds are for the most part exactly analogous to those of the corresponding derivatives of the monobasic acids and of oxalic acid.

A. Ethers of Carbonic Acid.

Ethyl carbonate, $CO(OC_2H_5)_2$, is formed:

1. **By the action of ethyl iodide upon silver carbonate;**

2. By the action of alcohol upon chloro-carbonic ether, and therefore indirectly from carbon oxychloride and alcohol:

$$CO(OC_2H_5)Cl + C_2H_5OH = CO(OC_2H_5)_2 + HCl.$$

It is a neutral liquid of agreeable odour, lighter than water and insoluble in the latter. B. Pt. 126°.

Analogous **Methyl-**, **Propyl-**, etc. **carbonates** are known, and also ethers containing two different alcohol radicles. It is a matter of no consequence which of these radicles is introduced first into the molecule, a proof of the equal valency of the two hydroxyls.

Ethyl-carbonic acid, $CO(OC_2H_5)(OH)$, corresponds exactly with ethyl-sulphuric, but is much less stable and only known in its salts.

Potassium ethyl-carbonate, $CO(OC_2H_5)(OK)$, results upon passing CO_2 into an alcoholic solution of potassium ethylate: $CO_2 + KOC_2H_5 = CO_3(C_2H_5)K$. It crystallizes in glancing mother-of-pearl plates, but is decomposed by water into potassium carbonate and alcohol.

B. Chlorides of Carbonic Acid.

Carbon oxy-chloride, *carbonyl chloride, phosgene*, $COCl_2$, (*J. Davy*). This compound is analogous to succinyl chloride, $C_2H_4(COCl)_2$, and to sulphuryl chloride, SO_2Cl_2. It is obtained by the direct combination of carbonic oxide and chlorine in sunlight, etc., and also by the oxidation of chloroform by means of chromic acid. Colourless gas, condensing to a liquid below +8°, of exceptionally suffocating odour. Soluble in benzene. As an acid chloride it decomposes violently with water into CO_2 and HCl. It therefore transforms hydrated acids into their anhydrides, with separation of water, and converts aldehyde into ethylidene chloride. It yields urea with secondary amines of the fatty series, and carbamic chlorides with secondary amines of the aromatic (B. 20, 783). Is employed in the preparation of dyes.

Chloro-carbonic acid, $COCl(OH)$, the acid chloride of carbonic acid analogous to chlor-oxalic acid (p. 249), has too great a tendency to break up into CO_2 and HCl to allow of its

existence either in the free state or in that of salts. As a monobasic acid, however, it forms ethers, *e.g.* **Chloro-carbonic ether,** $CO(Cl)(OC_2H_5)$ (= chloro-formic ether, $Cl—CO.OC_2H_5$), which results from the action of carbon oxy-chloride upon alcohol, (*Dumas*, 1833):

$$COCl_2 + C_2H_5OH = COCl(OC_2H_5) + HCl.$$

This is a volatile liquid of very pungent odour, which boils at 93°. It reacts as an acid chloride, being decomposed by water, and is therefore specially fitted to effect the synthetical entrance of the carboxyl group into many compounds.

The corresponding **Methyl-** etc. **ethers** are very similar.

C. Amides of Carbonic Acid.

The neutral amide of carbonic acid is urea or carbamide, the acid amide or aminic acid is carbamic acid. **Imido-carbonic acid,** $C(NH)^{OH}_{OH}$, would be an imide of carbonic acid, but it is only known in its derivatives, (*Sandmeyer*, B. **19**, 862).

The hypothetical form of cyanic acid, CO=NH (see table, p. 270), would also be an imide of carbonic acid, and that of cyanamide, $C(NH)_2$, a di-imide, while cyanic acid itself is to be regarded as a half nitrile, with cyanamide as its amide. The amidine of carbonic acid is guanidine. The "ortho-amide" of carbonic acid, which would possess the formula $C(NH_2)_4$, is unknown; when it might be expected to be formed, guanidine and ammonia result instead.

The modes of *formation* of urea and of carbamic acid are exactly analogous to those of the amides in general:

1. By the action of ammonia upon ethyl carbonate:

$$CO(OC_2H_5)_2 + 2NH_3 = CO(NH_2)_2 + 2C_2H_5.OH.$$
$$CO(OC_2H_5)_2 + NH_3 = CO(OC_2H_5)NH_2 + C_2H_5OH.$$

2. By the abstraction of the elements of water from carbonate or carbamate of ammonia. Dry carbon dioxide and ammonia combine together directly to ammonium carbamate, the

so-called anhydrous carbonate of ammonia, $CO(NH_2).OH, NH_3$, which goes into urea when heated to 135°, or when exposed to the action of an alternating current of electricity, thus:

$$CO(NH_2).OH,NH_3 = CO(NH_2)_2 + H_2O.$$

3. By the action of ammonia upon carbon oxy-chloride:

$$COCl_2 + 4NH_3 = CO(NH_2)_2 + 2NH_4Cl.$$
$$CO(OC_2H_5)Cl + 2NH_3 = CO(OC_2H_5)NH_2 + NH_4Cl.$$

Carbamic acid, $CO(NH_2)OH$. Carbamate of ammonia, which forms a white mass, dissociates at 60° into $2NH_3 + CO_2$. Its aqueous solution does not precipitate a solution of chloride of calcium at the ordinary temperature, since calcium carbamate is soluble in water, but, if it is heated, saponification into CO_2 and NH_3 ensues and calcium carbonate is thrown down.

Urethane, $CO(NH_2)(OC_2H_5)$, is the ethyl ether of carbamic acid. It is formed according to method 3, and by the direct union of cyanic acid with alcohol; also from urea nitrate and sodium nitrite in presence of alcohol. Large plates, easily soluble in water, etc. M. Pt. 47°–50°. Boils unchanged and acts as a soporific. One of its hydrogen atoms is replaceable by sodium. Urethane may be employed instead of cyanic acid for certain synthetic reactions (B. 23, 1856).

Analogous **Methyl-** etc. **ethers** of carbamic acid are also known. They are all readily saponified by alkalies into the alcohol, CO_2 and NH_3, and pass into urea when heated with ammonia.

Carbamic chloride, $CO\genfrac{}{}{0pt}{}{NH_2}{Cl}$ is obtained by the action of hydrochloric acid upon cyanic (*Wöhler*, A. 45, 357), and of $COCl_2$ upon NH_4Cl at 400°. It forms long, compact, colourless needles of pungent odour. M. Pt. 50°, B. Pt. 61°–62°. It reacts violently with water, amines, etc., and serves for the synthesis of organic acids (see these). Among its derivatives is *e.g.* **Dimethyl-carbamic chloride**, $CO[N(CH_3)_2]Cl$.

In the same way alkylated carbamic acids, $CO(NHR)OH$, which are only stable as ethers, have been prepared, *e.g.* **Ethyl-carbamic ether**, *ethyl-urethane*, $CO(NH.C_2H_5)(OC_2H_5)$, a liquid, B. Pt. 175°, which is formed *e.g.* by the direct combination of cyanic ether with alcohol at 100°.

Imido-dicarboxylic-diethyl ether, $NH(CO_2C_2H_5)_2$, is the imide corresponding to the amide urethane (cf. diacetamide). It results from the sodium compound of urethane and chloro-carbonic ether. Colourless crystals; M. Pt. 50°. By the exchange of one (OC_2H_5) group for NH_2, it gives rise to allophanic ether, and by the exchange of two, to biuret.

formed by the action of acid chlorides or anhydrides upon urea, or by the action of phosphorus oxy-chloride, $POCl_3$, upon a mixture of the latter with the acid. They correspond in their properties to di-acetamide (p. 198). To this class belong **Acetyl urea**, $CON_2H_3(C_2H_3O)$, and **Allophanic acid**, $CO(NH_2)(NH.CO_2H)$. Divalent monobasic acids also form ureides, not only in virtue of their alcoholic nature, but as alcohol and acid at the same time, thus :

Hydantoic acid, $CO<^{NH_2}_{NH.CH_2-CO_2H}$,

Hydantoïn, $CO<^{NH.CO}_{NH.CH_2}$, Lactyl urea, $CO<^{NH.CH-CH_3}_{NH.CO}$.

Hydantoïn or *glycolyl urea*, $C_3H_4N_2O_2$ (needles, neutral), and **Hydantoic acid** or *glycoluric acid*, $C_3H_6N_2O_3$ (prisms), are derivatives of glycollic acid ; the former goes, on saponification, into hydantoic acid, which in its turn is broken up into CO_2, NH_3 and glycocoll. They are obtained from certain uric acid derivatives (*e.g.* allantoïn) by the action of hydriodic acid, and also synthetically, for instance, hydantoic acid from glycocoll and cyanic acid. A **Methyl-hydantoïn**, $C_3H_3(CH_3)N_2O_2$, results from the gentle saponification of creatinine (p. 299), NH being here replaced by O.

For ureides of dibasic acids, see the uric acid group, p. 300.

Biuret, $NH<^{CO-NH_2}_{CO-NH_2} = C_2H_5N_3O_2$, is obtained by heating urea to 160° :

$$2NH_2.CO.NH_2 = NH_3 + NH(CO.NH_2)_2.$$

It crystallizes in white needles ($+H_2O$), readily soluble in water and alcohol. The alkaline solution gives a beautiful violet-red colouration on the addition of a little cupric sulphate,—the "biuret reaction." Biuret also results from the action of ammonia upon the **Allophanic ethers**, crystalline compounds sparingly soluble in water, which are prepared from urea and chloro-carbonic ethers, thus :

$$CO(NH_2)_2 + Cl.CO_2C_2H_5 = CO(NH_2)(NH.CO_2C_2H_5) + HCl.$$

Allophanic acid itself is not known in the free state, as it immediately breaks up into urea and carbon dioxide. Biuret may be regarded as its amide.

Carbonyl di-urea, $CO(NH.CO.NH_2)_2$. From carbon oxy-chloride and urea ; prisms.

D. Sulphur Derivatives of Carbonic Acid.

To most of the carbonic acid derivatives which have been described, there exist analogous compounds in which the oxygen is wholly or partially replaced by sulphur. Many of these again are unstable in the free state, from the fact of their being too readily saponifiable to CO_2, COS or CS_2, but they are known as salts or at least as ethers. The latter are often not real ethers, in so far that those which contain an alcoholic radicle linked to sulphur do not yield the corresponding alcohols on saponification (which is always easy), but mercaptans, in accordance with the intimate character of this linking.

Among these ethers there exist numerous isomers which cannot be described in detail here. Thus we are acquainted with two varieties of mono- and of dithio-carbonic ethers, and with isomers of thio- and dithio-carbamic ethers, as also of the alkylated thio-ureas (imido-carbamic acid derivatives). Of the acids which form the basis of these, only one form of each is known, as in the case of the cyanogen compounds; the remarks already made with respect to the constitution of the latter (p. 286, F.) apply here also.

The following summary gives the substances (part of them being only known as derivatives) which form the basis of these compounds :

	Tri-thiocarbonic acid,	$CS(SH)_2$
CS_2OH_2	Carbonyl di-thio-acid,	$CO{}^{SH}_{SH}$
	Di-thiocarbonic acid,	$CS{}^{SH}_{OH}$
CSO_2H_2	Carbonyl mono-thio-acid	$CO{}^{SH}_{OH}$
	Mono-thiocarbonic acid,	$CS{}^{OH}_{OH}$
	Thio-phosgene,	$CSCl_2$
	Thiocarbamic chloride,	$CS{}^{NH_2}_{Cl}$
CS_2NH_3	Di-thiocarbamic acid,	$CS{}^{NH_2}_{SH}$
	Imido-carbo-di-thio-acid,	$C(NH){}^{SH}_{SH}$
$CSONH_3$	Carbamine mono-thio-acid,	$CO{}^{NH_2}_{SH}$
	Mono-thiocarbamic acid,	$CS{}^{NH_2}_{OH}$
	Imido-carbo-mono-thio-acid,	$C(NH){}^{SH}_{OH}$
CSN_2H_4	Thio-carbamide,	$CS{}^{NH_2}_{NH_2}$
	Imido-carbamine thio-acid,	$C(NH){}^{NH_2}_{SH}$

Note.—The names of the compounds in this table are as nearly as possible literal translations from the German.

The above table shows that these compounds are of three kinds. The first contain the group =C=S, and are called "thiocarbonic" and "thiocarbamic" compounds; the second contain the group =C=O, and are termed "carbonyl" and "carbamine" compounds; while the third, which contain the group =C=NH, are the "imido-carbo" and the "imido-carbamic" compounds (cf. A **211**, 85).

The constitution is proved experimentally by the decomposition products obtained by the saponification of the isomeric compounds. Thus methyl thio-carbamide or methyl thio-urea, $CS(NH_2)(NH.CH_3)$ (white crystals), breaks up into CO_2, SH_2, NH_3 and methylamine, while the isomeric imido-carbamic thio-acid methyl ether or "imido-carbamine-thio-methyl," $C(NH)(NH_2)(S.CH_3)$, is decomposed into CO_2, $2NH_3$ and methyl mercaptan, or—when in the free state—into methyl mercaptan and cyanamide.

Thio-phosgene, *thiocarbonyl chloride,* $CSCl_2$. When chlorine is allowed to act upon carbon bisulphide, there is first formed the compound CCl_3SCl, which is converted into thio-phosgene by $SnCl_2$. Thio-phosgene is a red mobile strongly fuming liquid of sweetish taste, which attacks the mucous membrane; B. Pt. 68–74°. In its chemical behaviour it closely resembles phosgene, but is much more stable towards water than the latter, being only slowly decomposed even by hot water. It forms ammonium sulphocyanide—(not thio-urea)—with ammonia. (Cf. B. **20**, 2376; **21**, 337.)

Thiocarbonic acids. Tri-thiocarbonic acid is made up of the constituents $CS_2 + H_2S$, so that carbon bisulphide is its thio-anhydride, while the di-thiocarbonic acids contain the elements of $CS_2 + H_2O$ or of $COS + H_2S$, and the mono-acids those of $COS + H_2O$ or of $CO_2 + H_2S$. We find *accordingly that* CS_2 *combines with* Na_2S *to* CS_3Na_2, *with* KSC_2H_5 to $CS(SC_2H_5)SK$, *with* KOC_2H_5 (*i.e.* an alcoholic solution of potash) to $CS(OC_2H_5)SK$, potassium xanthate. In a similar manner COS and $CSCl_2$ combine with mercaptides and alcoholates.

Tri-thiocarbonic acid, *sulphocarbonic acid,* CS_3H_2, is a brown easily decomposable oil, insoluble in water, and its **ethyl ether,** $CS_3(C_2H_5)_2$, a liquid boiling at 240°.

Potassium Xanthate, $CS(OC_2H_5)SK$, (*Zeise*), whose preparation has been given above, crystallizes in beautiful colourless needles, very readily soluble in water, less so in alcohol. A solution of cupric sulphate throws down cupric xanthate as a yellow unstable precipitate, hence the name. It is employed in indigo printing.

With ethyl chloride, C_2H_5Cl, there is formed the neutral ether, $CS(OC_2H_5)(SC_2H_5)$. The free **Xanthic acid**, or *ethoxy-di-thiocarbonic acid*, $CS(OC_2H_5)SH$, is an oil insoluble in water which decomposes at so low a temperature as 25° into carbon bisulphide and alcohol.

Thio-carbamic acids. Di-thiocarbamic acid, $CS(NH_2)SH$, is formed as ammonia salt by the combination of CS_2 and NH_3 in alcoholic solution, (see p. 282):

$$CS_2 + 2NH_3 = CS(NH_2)SH, NH_3.$$

The free acid is a reddish oil which easily decomposes into thiocyanic acid and sulphuretted hydrogen:

$$CS(NH_2)SH = CSNH + SH_2.$$

Carbon bisulphide combines in an analogous manner with primary amines to form the aminic salts of alkylated di-thiocarbamic acids; thus ethylamine yields **ethylamine ethyl-di-thiocarbamate**, $CS(NH.C_2H_5)SH, NH_2C_2H_5$. When such salts are heated above 100°, H_2S is evolved and a di-alkyl-thio-urea left behind, *e.g.* **Diethyl-thio-urea**, $CS(NHC_2H_5)_2$; when $HgCl_2$ or $AgNO_3$ is added to their solutions, the Hg or Ag salts of the acids are precipitated, and these decompose on boiling with water into HgS or Ag_2S and the corresponding mustard oil, (cf. p. 283):

$$2CS(NHC_2H_5).SAg = 2CSNC_2H_5 + Ag_2S + H_2S.$$

Secondary amines also give rise to alkylated di-thiocarbamic acids, but the latter do not yield mustard oils, (p. 284).

Di-thio-urethane, $CS(NH_2)(S.C_2H_5)$, is the ethyl ether of di-thiocarbamic acid. As **Thio-urethane** is designated the ether $CO(NH_2)(S.C_2H_5)$, and as **Xanthamide** or *ethyl-thio-carbamide* its isomer $CS(NH_2)(OC_2H_5)$. **Methyl xanthamide** is thus $CS(NH.CH_3)(O.C_2H_5)$, and so on.

Thiocarbamide, *thio-urea*, *sulpho-urea*, $CS(NH_2)_2$, (*Reynolds*), is the analogue of urea, and its *modes of formation* are exactly analogous to those of the latter. Thus it is formed from ammonium thiocyanate just as urea is from the (iso)cyanate:

$$CSNH, NH_3 = CS(NH_2)_2.$$

To effect this molecular transformation a temperature of 130° is required, and it is only partial, since thiocarbamide goes back to a considerable extent into ammonium thiocyanate on being fused (see p. 282). It results further by the direct combination of sulphuretted hydrogen with cyanamide:

$$CN.NH_2 + SH_2 = CS(NH_2)_2.$$

Thiocarbamide crystallizes in rhombic six-sided prisms, or—if not quite pure—in long silky needles, readily soluble in water and alcohol. M. Pt. 172°. It is easily saponified to CO_2, H_2S and $2NH_3$. HgO abstracts H_2S from it, with formation of cyanamide. Cold permanganate of potash solution oxidizes it to urea. As a weak base it forms salts with acids, but at the same time it yields salts with HgO and similar bases; it also combines with salts, such as AgCl, $PtCl_4$, etc. When heated with alcoholic potash to 100°, it is reconverted into (the potassium salt of) thiocyanic acid and ammonia. Methyl iodide, CH_3I, reacts with it to produce imido-carbamine-thio-methyl, $C(NH)(NH_2)(S.CH_3)$, already mentioned at p. 296 (*Bernthsen* and *Klinger*).

Thio-urea comports itself in certain reactions as if it possessed the tautomeric constitutional formula of a hypothetical *imido-carbamine-thio-acid*, $C(NH)(NH_2)(SH)$. Thus, the constitution of the compounds which result from the action of halogen-alkyl upon thio-urea corresponds with this atomic grouping (see Imido-carbamine-thio-methyl, above).

Normal alkyl-thio-ureas also exist in large number. Many of these are broken up by hydrochloric or phosphoric acid into amine and iso-thiocyanate (p. 284).

Acid derivatives of thio-urea, *e.g.* **Acetyl-thio-urea**, are also known. To this class belongs, among other compounds, **Thio-hydantoïn**, which is however only to some extent analogous to the hydantoïn described on p. 294, since it is a derivative of the imido-carbamine-thio-acid and yields thioglycollic acid when decomposed, these reactions agreeing with the formula $C(NH)\langle{}^{NH-CO}_{-S-CH_2}$. It can be prepared synthetically and crystallizes in long needles.

E. Amidines of Carbonic Acid.

Guanidine, CH_5N_3, $= C(NH)(NH_2)_2$ (*Strecker*, 1861). This compound may also be termed imido-urea or imido-carbamide, thus: $O{=}C{=}(NH_2)_2$, urea; $(NH){=}C{=}(NH_2)_2$, guanidine.

Formation. By the oxidation of guanine (p. 306), also by heating cyanamide with ammonium iodide, and therefore from cyanogen iodide and ammonia:

$$CN.NH_2 + NH_4I = CN_3H_5, HI.$$

Preparation. By heating thio-urea with ammonium thiocyanate to 180°–190° and therefore from the thiocyanate alone at this temperature (*Volhard*):

$$CS(NH_2)_2 + NH_3.CNSH = C(NH)(NH_2)_2, CNSH + H_2S.$$

Guanidine is a very strong crystalline base, readily soluble in water and alcohol, which deliquesces in the air and absorbs carbonic acid, and combines with one equivalent of acid to form salts. **Guanidine carbonate**, $(CN_3H_5)_2, H_2CO_3$, crystallizes beautifully in quadratic prisms. Guanidine is readily saponifiable, at first to urea and ammonia, and finally to ammonia and carbon dioxide.

When the guanidine salts of fatty acids are heated, they pass into the characteristically crystallizing *Guanamines* (B. **25**, 534). By the action of a mixture of nitric and sulphuric acids upon guanidine nitrate, **Nitroguanidine**, $NH_2C(NH)NHNO_2$, is obtained, which is changed into **Amidoguanidine**, $NH_2C(NH)NHNH_2$, upon reduction. The latter, when boiled with alkalies or acids, breaks up into *Hydrazine*, N_2H_4, ammonia and carbon dioxide, and it yields with nitrous acid **Diazo-guanidine**, $NH_2C(NH)NHN=N.OH$, which in its turn is decomposed by alkalies into water, cyanamide and *Hydrazoic acid*, N_8H (p. 228). From amido-guanidine there can also be obtained the orange-yellow **Azo-dicarboxylic amide**, $NH_2CO—N=N—CONH_2$, and the colourless **Hydrazo-dicarboxylic amide**, $NH_2CO—NH—NH—CONH_2$ (p. 279), (*Thiele*, A. **270**, 1).

Numerous alkylated guanidines have been prepared by the action of ammonia, etc., upon alkyl thio-ureas, and by the combination of cyanamide with amines, etc. They break up on being heated with H_2S or CS_2, with reproduction of thio-ureas and amines (see Amidines, p. 200).

By the direct combination of cyanamide with glycocoll there is formed **Glycocyamine**, $C(NH)\begin{matrix}NH_2 \\ NH—CH_2—CO_2H\end{matrix}$, which gives up water with formation of **Glycocyamidine**, $C(NH)\begin{matrix}NH—CO \\ NH—CH_2\end{matrix}$. If, instead of glycocoll, its methyl derivative sarcosine is used, one obtains in an analogous manner creatine and creatinine (*Volhard*):

$$NH{=}C\left<\begin{matrix}NH_2 \\ N(CH_3)—CH_2—CO_2H\end{matrix}\right. \qquad NH{=}C\left<\begin{matrix}NH —— CO \\ N(CH_3)—CH_2\end{matrix}\right.$$

Creatine. Creatinine.

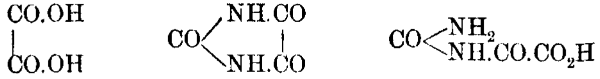
Creatine, $C_4H_9N_3O_2$ (*Chevreul*), is present in the juice of muscle and is prepared from extract of meat (*Liebig*). It crystallizes in neutral glancing prisms ($+ H_2O$) of a bitter taste, moderately soluble in hot water but only slightly in alcohol. When heated with acids it loses water and goes into:—

Creatinine, $C_4H_7N_3O$, which is an invariable constituent of urine, and which forms a characteristic double salt with zinc chloride, $2C_4H_7N_3O + ZnCl_2$. It is a strong base and much

more readily soluble in water and alcohol than creatine, into which it can be reconverted by taking up water. When mildly saponified, creatinine yields ammonia and methyl-hydantoïn, while creatine gives urea and sarcosine.

F. Uric Acid Group.

Just as the dibasic acids oxalic, malonic, tartronic and mesoxalic yield amides with ammonia, so can they react with the ammonia derivative, urea, to form compounds of an amidic nature. In such reactions either two molecules of water separate, so that no more carboxyl remains in the compound, or only one molecule is eliminated and a carboxyl group remains. In the former case the so-called "ureides" result, and in the latter the so-called "ureide-acids," *e.g.*, from oxalic acid, parabanic and oxaluric acids:



Oxalic acid. Ureide (parabanic acid). Ureide-acid (oxaluric acid).

In an analogous manner the ureide barbituric acid, $C_4H_4N_2O_3$, is derived from malonic acid, the ureide dialuric acid, $C_4H_4N_2O_4$, from tartronic acid, and the ureide alloxan, $C_4H_2N_2O_4$, and ureide-acid alloxanic acid, $C_4H_4N_2O_5$, from mesoxalic acid.

These are solid and, for the most part, beautifully crystallizing compounds of a normal amidic character, and therefore easily broken up backwards by saponification into urea (or CO_2 and NH_3) and the respective acid. The ureide-acids may be regarded as half-saponified ureides, resulting in fact from the latter in this manner.

Analogous compounds are also derived from the aldehydic- or alcoholic-acids, glyoxalic acid, $CH(OH)_2—CO_2H$, and glycollic acid, $CH_2(OH)—CO_2H$; from the former allanturic acid, $C_3H_4N_2O_3$, and from the latter the ureide hydantoïn and the ureide-acid hydantoic acid, (see p. 294). They show, however, a somewhat different behaviour on saponification. In addition

to these so-called "mono-ureides" there exist also "di-ureides," *i.e.*, compounds into whose composition two molecules of urea have entered. These are uric acid, $C_5H_4N_4O_3$, and its near relations xanthine, $C_5H_4N_4O_2$, theobromine, $C_5H_2(CH_3)_2N_4O_2$, caffeine, $C_5H(CH_3)_3N_4O_2$, hypoxanthine, $C_5H_4N_4O$, and guanine, $C_5H_5N_5O$; further, purpuric acid, $C_8H_5N_5O_6$, alloxantin, $C_8H_4N_4O_7$, allantoïn, $C_4H_6N_4O_3$, and other compounds.

Many of these di-ureides occur in nature. Uric acid is contained in the urine, blood and muscle juice of the carnivora, in gravel and chalk stones, in guano, and in the excrementa of serpents; xanthine in small quantity in the urine, blood and liver, and sometimes in gravel, almost always together with hypoxanthine; guanine in guano; and carnine in extract of meat. Theobromine is present in the cocoa bean (Theobroma Cacao), and caffeine in the coffee bean, in tea, in Paraguay tea (Ilex paraguayensis), and in the guarana (the fruit of Paullinia sorbilis), etc.

Many of these compounds are nearly related to one another; thus we have hypoxanthine formed by the action of sodium amalgam upon uric acid, (taking away of O), xanthine by the action of nitrous acid upon guanine, (exchange of N and H for O), theobromine and caffeine by the methylation of xanthine, and hypoxanthine by the action of nitric acid upon carnine.

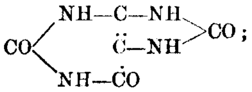
Formation. The ureides mentioned above or other diureides result, frequently together with urea, by the oxidizing decomposition (or oxidation) of the diureides which have been enumerated.

Thus uric acid yields allantoïn with water and PbO_2 and either purpuric acid, alloxan, alloxantin or parabanic acid with nitric acid, according to the conditions, while caffeine yields dimethyl-alloxan and methyl-urea with chlorine. These decomposition products also stand in an intimate relation to one another, *e.g.*, alloxan gives alloxantin, dialuric acid and barbituric acid on reduction; hydantoïn results *e.g.* from the oxidation of alloxanic acid and is itself oxidized to allanturic acid; while dialuric acid and alloxan combine to alloxantin with elimination of water, etc., etc.

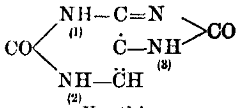
Some of these ureides have also been prepared synthetically from urea and the requisite acid, phosphorus oxy-chloride having proved itself to be particularly useful as a dehydrating agent in such cases; in this way parabanic acid has been obtained from oxalic, and barbituric

acid from malonic. Uric acid may be synthetized by heating glycocoll with urea, and also indirectly from aceto-acetic ether and urea, methyl-uracyl being formed as intermediate product; therefore also xanthine, theobromine and caffeine indirectly.

The *constitution* of the simpler ureides and ureide-acids follows directly from their decomposition products, syntheses and relations to one another, while considerations of a more complex nature have led to the constitution of uric acid, (*Medicus*), and of xanthine and its more nearly allied compounds, (*E. Fischer*, A. 215, 253):



Uric acid.



Xanthine.

Guanine is imido-xanthine (O being replaced by NH); theobromine and caffeine are di- and trimethyl-xanthines (the H atoms 1 and 3, or 1, 2 and 3 being replaced by CH_3). From this it follows that uric acid is the di-ureide of the unknown compound, $C(OH)_2{=}C(OH){-}CO_2H$, or of the hydrate of tartronic acid, $C(OH)_3{-}CH(OH){-}COOH$.

Most of the ureides and di-ureides have the character of more or less strong acids.

Since this acid character is not to be explained, as in the case of the ureide-acids, by the presence of carboxyl, one must assume that it depends upon reasons similar to those which apply in the case of cyanic acid and of succinimide, viz., that the replaceable hydrogen atoms are imido-hydrogen atoms whose chemical nature is determined by the surrounding carbonyl groups. This explains, for instance, why parabanic acid is a strong dibasic acid.

Only a few of the more important among these compounds can be discussed here. (Cf. *Liebig* and *Wöhler*, A. 26, 241; *Baeyer*, A. 127, 1, 199; 130, 129, etc.)

Parabanic acid,* $CO<\begin{matrix}NH.CO\\ |\\ NH.CO\end{matrix}$, is prepared by the action of nitric upon uric acid, and crystallizes in needles or prisms soluble in water and alcohol. The salts, *e.g.*, $C_3HKN_2O_3$, $C_3Ag_2N_2O_3$, are unstable, being converted by water into salts of the monobasic **Oxaluric acid**, $CO<\begin{matrix}NH_2\\ NH.CO.CO_2H\end{matrix}$, which crystallize well.

* *Oxalyl-urea.*

A **Methyl-parabanic acid**, $CO\Big\langle\begin{matrix}N(CH_3)-CO\\ NH\ \text{——}\ CO\end{matrix}$, and a **Di-methyl-parabanic acid**, the so-called "**Cholestrophane**," $CO\Big\langle\begin{matrix}N(CH_3)-CO\\ N(CH_3)-CO\end{matrix}$, are also known. The former is prepared *e.g.* by the action of nitric upon methyl-uric acid and crystallizes in prisms, while the latter is obtained from theine with nitric acid, chlorine water, etc., and also by the methylation of parabanic acid, *i.e.* from the Ag salt and CH_3I. It crystallizes in plates and distils without decomposition.

Methyl-uracyl, $CO\Big\langle\begin{matrix}NH-C(CH_3)\\ NH-CO\end{matrix}\Big\rangle CH$, is produced by the action of urea upon aceto-acetic ether, water and alcohol being eliminated here (*Behrend*, A. **229**, 1). When it is treated with nitric acid, a nitro-group enters the molecule, and the methyl-group is oxidized to carboxyl, thus forming:

Nitro-uracyl-carboxylic acid, $CO\Big\langle\begin{matrix}NH-C(CO_2H)\\ NH-CO\end{matrix}\Big\rangle C(NO_2)$. This, in its turn, can give up carbon dioxide and pass into:

Nitro-uracyl, $CO\Big\langle\begin{matrix}NH-CH\\ NH-CO\end{matrix}\Big\rangle C(NO_2)$, which yields, upon reduction, amido-uracyl and

Iso-barbituric acid, *Oxy-uracyl*, $CO\Big\langle\begin{matrix}NH-CH\\ NH-CO\end{matrix}\Big\rangle C.OH$. This last is oxidized by bromine water to:

Iso-dialuric acid, doubtless $CO\Big\langle\begin{matrix}NH-C(OH)\\ NH-CO\end{matrix}\Big\rangle C(OH)$, from which, upon warming with urea and sulphuric acid, uric acid is synthetized (cf. p. 305).

Barbituric acid, *malonyl urea*, $C_4H_4N_2O_3$, is a dibasic acid, crystallizing in large colourless prisms ($+ 2H_2O$). It is the H-atoms of the methylene group, CH_2, and not of the imido-group which are replaceable, since dimethyl-malonyl-urea, which can be prepared from the silver salt and methyl iodide, does not yield malonic acid when boiled with alkalies, but dimethyl-malonic acid, $(CH_3)_2{=}C(CO_2H)_2$.

Dialuric acid, *tartronyl urea*, $C_4H_4N_2O_4$. Strong dibasic acid. Crystallizes in colourless needles or prisms which redden in the air and go into alloxantin upon oxidation.

Alloxan, *mesoxalyl urea*, $CO\Big\langle\begin{matrix}NH-CO\\ NH-CO\end{matrix}\Big\rangle CO$. Prepared from uric acid and cold HNO_3. Large colourless glancing

rhombic prisms (+ $4H_2O$), strongly acid and readily soluble in water. Colours the skin purple-red. Ferrous sulphate produces an indigo blue colour with its solution. It combines with $NaHSO_3$ and readily changes into alloxantin. The corresponding "ureide-acid," **Alloxanic acid**, $C_4H_4N_2O_5$, which alloxan yields even with cold alkali, forms a radiating crystalline mass readily soluble in water. **Methyl- and Dimethyl-alloxan** are also known, being obtained by the action of nitric acid upon methyl-uric acid and caffeine respectively.

The di-ureide **Alloxantin**, $C_8H_4N_4O_7$, stands mid-way in composition between tartronyl- and mesoxalyl-urea, by the combination of which it is formed.

One obtains it by acting on alloxan with H_2S or directly from uric acid and HNO_3. It crystallizes in small hard prisms (+ $3H_2O$), which become red in air containing ammonia, their solution acquiring a deep blue colour on the addition of Fe_2Cl_6 and NH_3. The tetra-methyl derivative, **Amalic acid**, $C_8(CH_3)_4N_4O_7$, results from theine and chlorine water, and forms colourless crystals which redden the skin and whose solution is turned violet-blue by alkali. Both these compounds yield, upon oxidation, first alloxan or its di-methyl derivative, and then parabanic or dimethyl-parabanic acid. Thus alloxantin has perhaps the constitution :

$$CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>C(OH)-O-CH<\begin{matrix}CO-NH\\CO-NH\end{matrix}>CO.$$

When heated with ammonia it is converted into **Murexide**, the acid ammonium salt of **Purpuric acid**, $C_8H_5N_5O_6$(+ H_2O), perhaps $CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>C(OH)-NH-CH<\begin{matrix}CO-NH\\CO-NH\end{matrix}>CO$, which is formed when uric acid is evaporated with dilute nitric acid, and ammonia added to the residue ; this is the "murexide test" for uric acid.

Murexide crystallizes in four-sided tables or prisms (+ H_2O) of a golden-green colour, which dissolve to a purple-red solution in water and to a blue one in potash. The free acid is incapable of existence.

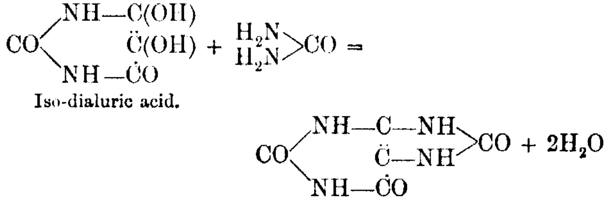
Allantoïn is a di-ureide of glyoxalic acid, of the constitution $CO<\begin{matrix}NH-CH-NH\\NH-\overset{|}{C}O\quad NH_2\end{matrix}>CO$, which is found in the allantoic liquid of the cow, the urine of sucking calves, etc. It forms

glancing prisms of neutral reaction, yields salts with alkalies, and can be prepared synthetically from its components.

Uric acid, $C_5H_4N_4O_3$, (*Scheele*, 1776). For occurrence and synthesis, see pp. 301 and 303.

Synthesis. 1. By heating glycocoll with urea (*Horbaczewski*, B. **15**, 2678).

2. By heating iso-dialuric acid with urea and concentrated sulphuric acid (*R. Behrend* and *O. Roosen*, A. **251**, 235):



Iso-dialuric acid.

Uric acid.

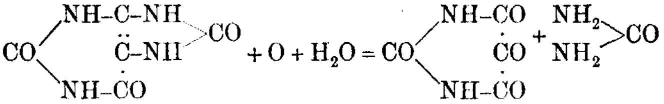
3. By heating cyan-acetic acid with urea (B. **24**, 3419).

Preparation. It is prepared from guano and the excrement of serpents, and crystallizes in small tables. Almost insoluble in water and insoluble in alcohol and ether, but concentrated sulphuric acid dissolves it without decomposition, and from this solution it is thrown down unchanged by water. For the murexide reaction, see above. Uric acid is a weak dibasic acid; its common salts are the primary (*i.e.*, hydrogen) ones, *e.g.* $C_5H_3KN_4O_3$, a powder sparingly soluble in water.

When the two lead salts are treated with methyl iodide, **Methyl**- and **Dimethyl-uric acid** are obtained, both of which also are weak dibasic acids, since they still contain replaceable imido-hydrogen atoms.

Constitution. The constitutional formula, given above, was first proposed by *Medicus*, and afterwards proved to be correct by *E. Fischer* (A. **215**, 253). His researches on the subject were of a difficult nature, but the following is a summary of their most important results:—(1) Uric acid yields alloxan and urea when cautiously oxidized, this proving that we have to deal here with a carbonic acid derivative and a carbon chain, C—C—C; (2) Uric acid contains four imido-groups (see Dimethyl-uric acid), since, by the introduction of four methyl groups, one after the other, all the four nitrogen atoms are

separated as methylamine; (3) Dimethyl-uric acid yields methyl-alloxan and methyl-urea on oxidation, thus:



Xanthine, $C_5H_4N_4O_2$, is produced from guanine and nitrous acid, and *from uric acid and sodium amalgam. It is a white amorphous mass*, and is at the same time base and acid; thus it yields *e.g.* the lead compound $C_5H_2PbN_4O_2$, which is converted into theobromine by methyl iodide.

Hypoxanthine, *sarcine*, $C_5H_4N_4O$. Sparingly soluble in water and very like xanthine.

Theobromine, $C_7H_8N_4O_2$. Crystalline powder of bitter taste, sparingly soluble in water and alcohol. Forms salts both as base and as acid. The silver salt, $C_7H_7AgN_4O_2$, yields caffeine when treated with CH_3I, (*Strecker*, *Fischer*).

Caffeine or **Theine**, $C_8H_{10}N_4O_2$. Crystallizes $(+ H_2O)$ in beautiful long glancing silky needles of faintly bitter taste, which are sparingly soluble in cold water and alcohol, and can be sublimed. The salts are readily decomposed by water. Chlorine breaks it up into dimethyl-alloxan and mono-methyl-urea.

Guanine, $C_5H_5N_5O$. White amorphous powder insoluble in water but soluble in ammonia. It is a divalent base, but also forms salts with bases. Yields guanidine, parabanic acid and carbon dioxide with $KClO_3$ + HCl. Is an imide of xanthine, containing NH instead of O, and hence nitrous acid converts it into the latter compound.

Adenine, $C_5H_5N_5$, which is a polymer of hydrocyanic acid, is a base which results from the decomposition of nucleïn (see this); it has been obtained from the pancreatic glands of oxen and from tea leaves. It crystallizes in long needles and is converted by nitrous acid into hypoxanthine, whose imide it therefore is.

Carnine. A powder rather easily soluble in hot water.

XIV. CARBOHYDRATES.

Most of the carbohydrates which occur in nature have been known for a long time. Cane sugar was found in the sugar beet by *Marggraf* in 1747, and dextrose in honey by *Glauber*. The transformation of starch into sugar (p. 320) was first observed by *Kirchoff* in 1811.

The name "carbohydrate" was formerly applied in particular to three groups of compounds nearly allied to one another and which are very widely distributed in nature, viz., those of grape sugar, $C_6H_{12}O_6$, of cane sugar, $C_{12}H_{22}O_{11}$, and of cellulose, $(C_6H_{10}O_5)_n$. All of them contain 6 atoms of carbon or some multiple of 6, and hydrogen and oxygen in the same proportion in which these elements are present in water. They are nearly related to the hexatomic alcohols, $C_6H_{14}O_6$, from which they are respectively derived by the abstraction of H_2 or of $H_2 + H_2O$.

The carbohydrates of the grape sugar group, the hexoses, are distinguished from the hexatomic alcohols, $C_6H_{14}O_6$, by containing two atoms of hydrogen less in the molecule; chemically they are aldehyde-alcohols or ketone-alcohols (see p. 309).

The compounds of the cane sugar and cellulose groups are derived from those of the grape sugar group by the elimination of the elements of water from the latter, and they are anhydrides or ethereal derivatives of these.

The name carbohydrate has, however, acquired a much wider significance during the last few years, because on the one hand numerous isomers of grape sugar—hexoses—have been discovered and, in part, prepared synthetically; while on the other hand we have also become acquainted with aldehyde-alcohols, *i.e.*, sugar varieties poorer in carbon (especially the pentoses, $C_5H_{10}O_5$, which are widely distributed in nature, tetrose, $C_4H_8O_4$ [B. 25, 2549], and glycerose, $C_3H_6O_3$), and with others richer in carbon, which have been synthetized,—heptoses, octoses, and nonoses. All of these contain two atoms of hydrogen less in the molecule than the corresponding polyatomic alcohols.

These compounds might therefore be described in connection with the aldehyde- and ketone-alcohols (p. 237), of which glycollic aldehyde is the

first member. On account, however, of the many peculiarities which they possess, it has been preferred to treat them separately.

The carbohydrates show many characteristic reactions, which will be referred to under the individual groups. They give, for example, a beautiful deep violet colouration with α-naphthol and concentrated sulphuric acid (*Molisch*, B. **19**, Ref. 746).

A. Pentoses.

The pentoses are characterized, among other things, by the fact that they yield furfurol or methyl-furfurol upon prolonged boiling with hydrochloric acid, water being eliminated; this reaction allows of their quantitative estimation (B. **24**, 3577). Arabinose gives furfurol itself, while its homologue rhamnose gives methyl-furfurol. Upon warming with hydrochloric acid and phloroglucin, cherry-red colourations are produced. The pentoses are not fermentable, and they yield characteristic compounds with phenyl-hydrazine (see Hexoses); unlike the hexoses they have not as yet been synthetized.

1. **Arabinose**, $C_5H_{10}O_5 = CH_2OH—CH(OH)_3—CHO$, is produced by boiling gum-arabic, cherry gum, or beetroot chips with dilute sulphuric acid, and forms dextro-rotatory prisms. It takes on hydrocyanic acid, and thus yields the cyanides of two stereo-isomeric oxy-acids, which are derived from normal caproic acid, viz., *l*-mannonic acid (*Kiliani*, B. **20**, 339, 1233) and *l*-gluconic acid (*E. Fischer*). The corresponding alcohol is arabite.

2. **Xylose**, *wood sugar*, $C_5H_{10}O_5$, is prepared by boiling wood-gum (which see), straw and jute with dilute sulphuric acid, and is very similar to arabinose. For its constitution, see B. **24**, 537. The corresponding alcohol is xylite.

3. **Ribose**, $C_5H_{10}O_5$, is stereo-isomeric with arabinose (B. **24**, 4214).

Homologues. 4. **Rhamnose**, *iso-dulcite*, $C_6H_{12}O_5 = C_5H_9O_5(CH_3)$, is obtained from several glucosides, *e.g.* quercitrin (which see), or xanthorhamnin (yellow needles, present in French berries, Rhamnus tinctoria, etc.), by the action of dilute sulphuric acid. Colourless crystals ($+ H_2O$); M. Pt. 93°. For constitution, see *Fischer* and *Tafel*, B. **20**, 1091; **21**, 1657, 2173).

5. **Fucose**, isomeric with rhamnose. Obtained from sea-weed. (Cf. A. **271**, 86.)

B. The Grape Sugar Group, $C_6H_{12}O_6$.

(*Hexoses* or *Glucoses.*)

The glucoses are sweet and for the most part crystalline compounds easily soluble in water, sparingly soluble in absolute alcohol and insoluble in ether. They possess the character of pentavalent aldehyde- or ketone-alcohols and closely resemble mannite, etc., but differ from it in having strongly reducing properties, in their behaviour towards phenyl-hydrazine, and in certain cases also by being fermentable by germinating yeast. Like tartaric acid they exist in optically active isomeric modifications, one of which turns the plane of polarization of light to the right and another to the left, while the third is inactive, being produced by the union of the two active modifications. We thus distinguish between dextro-, lævo-, and inactive-mannose, and designate the glucoses, fructoses, etc., which are genetically related to them, as belonging to *d*-, *l*-, or *i*- series (without reference to their actual rotation).

Formation. 1. The hexoses are produced, both in plants and artificially, from the carbohydrates of the cane sugar and starch groups by the taking up of water, this being brought about either by the action of enzymes or by boiling with very dilute acids, especially hydrochloric (see pp. 317 and 320).

2. *Synthesis of hexoses.* By the action of lime-water upon trioxymethylene (p. 147), *Butlerow* obtained the so-called "methylenitan," a mixture of several substances, one of which is acrose (see below). *O. Loew* obtained formose in a similar manner from formic aldehyde and milk of lime, this being likewise a mixture containing a true glucose (acrose).

E. Fischer and *Tafel* then succeeded in synthetizing two sugar varieties, *α*- and *β*-acrose, the first of which is identical with *i*-fructose, by the action of baryta water upon acrolein bromide or crude glycerine aldehyde ("glycerose," obtained by oxidizing glycerine with bromine and soda). Cf. *E. Fischer*, B. **23**, 2114, *et seq.*

From *α*-acrose, as the starting point, a number of other glucoses have been prepared. By fermenting it with yeast, *l*-fructose is isolated, the *d*-fructose (lævulose) alone undergoing decomposition. Sodium amalgam,

on the other hand, converts it into *i*-mannite, which in its turn yields *i*-mannose upon oxidation with nitric acid. From this latter the *l*-modification is obtainable by fermentation. The further oxidation of *i*-mannose produces *i*-mannonic acid. This last can then be split up into the *d*- and *l*-modifications by means of the strychnine or brucine salts; the first of these, *d*-mannonic acid, is also got by the oxidation of the natural *d*-mannite; while the second, *l*-mannonic acid, can be prepared (together with *l*-gluconic acid, which see) by the taking up of hydrocyanic acid by arabinose, etc. All three mannonic acids have been reduced by sodium amalgam to the corresponding *d*-, *l*- and *i*-mannoses (*E. Fischer*, B. **22**, 2204).

Now the three mannonic acids can be converted into *d*-, *l*- and *i*-gluconic acids (p. 236); and, upon reduction with sodium amalgam, *d*- and *l*-gluconic acids give *d*- and *l*-glucoses, of which the first is identical with natural grape sugar. By the union of *d*- with *l*-glucose, *i*-glucose is obtained, and by the reduction of *d*-glucose, the sorbite found in nature. *d*-fructose yields a mixture of *d*-mannite and sorbite when reduced.

Further, the reduction of mucic acid yields *i*-galactonic acid, and the reduction of the latter *i*-galactose, which gives *l*-galactose upon fermentation.

Gulose (whose name is intended to express the relationship with glucose) can be prepared synthetically from gulonic acid. Hydrocyanic acid adds itself on to xylose with the (ultimate) formation of *l*-gulonic acid, which yields *l*-gulose on reduction. By the reduction of ordinary saccharic acid, *d*-gulonic acid is obtained, and this leads to *d*-gulose. A mixture of these two hexoses then gives *i*-gulose. Lastly, the reduction of talose yields talonic acid, which is also obtainable (p. 236) by the molecular transformation of galac tonic acid (*E. Fischer* and his pupils, B. **24**, 526, 3625; **25**, 1031, 1247).

For the genetic relations of these compounds, see table, p. 311.

The synthesis of heptoses, octoses, etc., depends upon the property of the hexoses to unite—like aldehyde—with hydrocyanic acid to nitriles, which yield hexatomic-monobasic acids upon saponification, the latter being then reducible to the corresponding aldehydes (heptoses). These can in their turn be transformed in the same manner (see also p. 313).

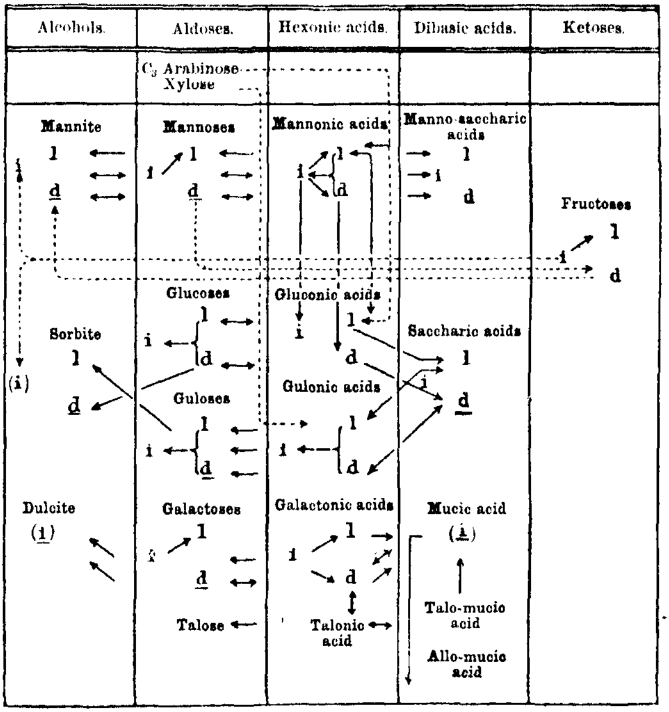
Thus, from mannose, $C_6H_{12}O_6$, there is obtained mannose-carboxylic acid, $C_6H_7(OH)_6(CO_2H)$, and, from the latter, **Manno-heptose**, $C_6H_7(OH)_6(CHO)$; from this we proceed to **Manno-octose** and **Manno-nonose**. Similarly glucose leads to **Gluco-heptose**, galactose to **Gala-heptose**, etc.

Rhamnose (Methyl-pentose) yields **Rhamno-hexose**, $C_6H_{11}(CH_3)O_6$, **Rhamno-heptose**, and **Rhamno-octose** in an analogous manner.

See table on following page.

Behaviour. 1. Fermentation. Most of the hexoses are fermentable. They ferment with yeast, undergo the lactic or butyric fermentation with the respective bacteria, and are transformed under certain conditions into mucous dextrine-like substances by the "mucous" fermentation.

SUMMARY OF GENETIC RELATIONS.



Among others, d-mannose, d-glucose, d-fructose and *d*-manno-nonose are fermentable, but not *d*-manno-heptose or -octose, or the pentoses; *l*-glucose, *l*-mannose and *l*-fructose do not ferment with yeast, perhaps because the cells of the fungus have become accustomed to the *d*-compounds occurring in nature.

2. The hexoses are readily oxidizable, and they therefore reduce an ammoniacal silver solution, and also *Fehling's* solution if warmed with it. By careful oxidation the mannoses, glucoses, and galactose yield the hexonic acids mentioned in the above table. When the oxidation proceeds further, glucose gives saccharic, tartaric and oxalic acids, and galactose gives mucic

The common derivation of the mannoses and glucoses from arabinose (see Mannonic and Gluconic acids) shows that their stereo-isomerism depends upon the asymmetry of the second, *i.e.* the (α) carbon atom. This also follows, among other reasons, from the identity of the osazones of the mannoses and glucoses. They belong, however, to the class of stereo-isomers which do not unite with one another (see p. 236). The galactoses and taloses are similarly related, since they yield the same osazones.

To the fructoses, on the contrary, there are no corresponding mannonic or gluconic acids; they are not aldehydic but ketonic alcohols, receive the generic name of **Ketoses**, and have the formula:

$$CH_2(OH)—CH(OH)—CH(OH)—CH(OH)—CO—CH_2(OH).$$

That, like the aldoses, they act as reducing agents, is in agreement with the general character of the ketone-alcohols.

In accordance with the above formulae the hydrazones of the two classes of compounds are different, but the osazones are identical, thus:

$$\begin{array}{ll} CH_2OH—[CH(OH)]_3—C & —CH \\ \qquad\qquad\qquad\qquad \Vert & \ \ \Vert \\ \qquad\qquad\qquad\quad N_2HC_6H_5 & N_2HC_6H_5. \end{array}$$

The atomic group $CH_2(OH)—[CH(OH)]_3—$ is therefore the same in the mannoses, glucoses and fructoses, but upon its internal structure depends whether they belong to the *d*-, *l*-, or *i*- class of compounds (*stereo-isomerism*).

Cf. also *Skraup*, M. f. Ch. **10**, 401; *Erwig* and *Koenigs*, B. **22**, 2207.

Tollens regards the hexoses as intramolecular anhydrides (of the nature of ethylene oxide) of aldehydic and ketonic hydrates. Cf. also B. **22**, 2207.

For further details as to the configuration of the hexoses (which is now settled in the case of the glucoses, mannoses, guloses and fructoses), see *E. Fischer*, B. **24**, 2683. Leaving out of account optically inactive forms, there are sixteen stereo-isomeric aldoses possible according to theory, and nine of these are known at present.

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1. ***d*-Glucose**, *Grape sugar* or *Dextrose*, $C_6H_{12}O_6 + H_2O$, occurs along with *d*-fructose in most sweet fruits, also in diabetic urine, etc. etc.

It is prepared from other carbohydrates, as given at pp. 309 and 317. The sugar which is obtained from starch and termed starch sugar contains, in addition to dextrose, dextrine and unfermentable substances. It crystallizes from water in granulous masses made up of six-sided plates which melt at 86°, and from

methyl alcohol in small anhydrous prisms free from water; M. Pt. 146°. It is dextro-rotatory, hence the name "dextrose."

A freshly prepared solution turns the plane of polarization almost twice as much as one which has been kept or heated to boiling, a phenomenon which is known as "bi- or multi-rotation." This is probably due to the formation of hydrates having a different rotatory power (A. **272**, 170). For the estimation of grape sugar by means of *Fehling's* solution, see *e.g.* J. pr. Ch. [2] **21**, 254; cf. also B. **23**, 3003.

d-**Glucose-phenyl-hydrazone,** $C_{12}H_{18}N_2O_5$, forms fine crystals which melt at 115°. Another modification melts at 144°.

d-**Phenyl-glucosazone** crystallizes in sparingly soluble needles (B. **17**, 579). Nascent hydrogen reduces it to iso-glucosamine, which yields *d*-fructose with nitrous acid.

The rotation produced by the hydrazones and osazones may be the opposite of that of the mother substance. It is an important point for the recognition of the latter.

d-**Pentacetyl-glucose,** $C_6H_7O(OC_2H_3O)_5$. M. Pt. 111°.

d-**Glucosone,** $CH_2(OH)—[CH(OH)]_3—CO—CHO$ (see p. 312), forms a syrup which does not ferment with beer yeast, and which yields the osazone immediately with phenyl-hydrazine.

l-**Glucose.** This resembles *d*-glucose closely, excepting that it turns the plane of polarization as strongly to the left as the latter does to the right.

i-**Glucose.** From *i*-gluconic acid. A colourless syrup. The osazone, *i*-glucosazone, melts at 216°, and, apart from rotatory power, is deceptively like the *d*- and *l*-osazones.

2. *d*-**Mannose,** $C_6H_{12}O_6$, which is stereo-isomeric with *d*-glucose, results together with *d*-fructose from the cautious oxidation of mannite, also by boiling the reserve-cellulose of the seed of the Brazil-nut with dilute hydrochloric acid, and by reducing mannonic acid with sodium amalgam. It forms a colourless amorphous mass readily soluble in water. It rotates less strongly to the right than *d*-glucose, and yields the same osazone. When treated with sodium amalgam it passes readily into *d*-mannite. The hydrazone (M. Pt. 195°) is difficultly soluble in water.

i-**Mannose** forms a colourless syrup. Its hydrazone is optically inactive. The osazone is identical with that from *i*-fructose.

3. **Guloses.** These are colourless syrups, either unfermentable or only

fermentable with difficulty. The osazones are different from the glucosazones. For their relation to the glucoses, see B. **24**, 522.

4. *d*-**Galactose**, $C_6H_{12}O_6$, is produced along with *d*-glucose from milk sugar and dilute acid. It is found in the cerebrin of the brain. Fine needles, M. Pt. 163°; dextro-rotatory. It yields a pentacetyl compound which melts at 142° (cf. B. **22**, 2207), and gives mucic acid upon oxidation.

5. **Talose**. A syrup. The phenyl-hydrazone is very readily soluble in water (difference from galactose).

6. *d*-**Fructose**, *Fruit sugar* or *Lævulose*, $C_6H_{12}O_6$, is almost invariably found along with *d*-glucose in the juice of sweet fruits and also, together with the latter, in honey. It is formed along with *d*-glucose by the inversion of cane sugar, and together with *d*-mannose by the cautious oxidation of *d*-mannite; also from *d*-phenyl-glucosazone and therefore indirectly from *d*-glucose (see p. 315); and it is easily prepared by heating inulin with very dilute acid (B. **23**, 2084). It crystallizes with difficulty in hard, anhydrous, rhombic crystals of M. Pt. 95°. It is lævo-rotatory, although belonging genetically to the *d*-series. Its power of rotation is almost double that of *l*-glucose.

l-**Fructose** is the *l*-modification of ordinary fruit sugar. It therefore rotates in the opposite direction, *i.e.* is dextro-rotatory.

i-**Fructose**, *α-Acrose*, $C_6H_{12}O_6$. This is formed synthetically, together with *β*-acrose, from glyceric aldehyde, and from formic aldehyde, as given on p. 309. A syrup. It is re-obtained from its osazone, *α*-**Acrosazone** (M. Pt. 217°), by the conversion of the latter into *α*-**Acrosone** by means of hydrochloric acid (analogously to the formation of glucosone), and reduction of this with zinc dust and acetic acid.

7. **Sorbinose**, *Sorbin*, $C_6H_{12}O_6$, is present in the juice of the service-berry. Crystalline. It belongs to the ketoses, since it yields trioxy-glutaric acid and no hexonic acid upon oxidation.

Inosite (p. 427), a benzene derivative, is isomeric with sorbin.

For sugars richer in carbon, see *E. Fischer*, A. **270**, 64; **272**, 186.

C. The Cane Sugar Group, $C_{12}H_{22}O_{11}$.

To the cane sugar group belong all the compounds of the formula, $C_{12}H_{22}O_{11}$, which are converted into glucoses, $C_6H_{12}O_6$, by the action of dilute acids; also raffinose, $C_{18}H_{32}O_{16} + 5H_2O$, which shows a similar chemical behaviour. The compounds of the cane sugar group possess for the most part a sweet taste, and they crystallize more readily and are more stable than the hexoses, but resemble the latter in solubility. They are optically active. With the exception of maltose they are not directly fermentable, but only after being broken up (see below). Cane sugar does not reduce *Fehling's* solution, but milk and malt sugars do. They are split up into hexoses, with assimilation of water, when boiled with dilute mineral acids or when subjected to the action of enzymes (diastase and soluble yeast ferment, see p. 322).

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

Cane sugar is broken up in this way into two molecules of *d*-glucose and *d*-fructose, milk sugar into *d*-glucose and galactose, and maltose into two molecules of *d*-glucose.

On account of this breaking down of the molecule, the sugars of the above group are termed "*-bioses*," *e.g.* milk sugar is lactobiose. Similarly raffinose is a "*-triose*," Mele-triose. This decomposition with assimilation of water is termed *hydrolysis* or—especially in the case of cane sugar—*inversion*, and the lævo-rotatory mixture, so obtained, invert-sugar, because the original dextro-rotatory action upon polarized light has been reversed.

Constitution. The compounds of the cane sugar group are thus ethereal anhydrides of the hexoses, *e.g.* cane sugar is *d*-glucose-*d*-fructose anhydride, and malt sugar *d*-glucose anhydride, etc. In this formation of anhydride there remain four hydroxyls over for every six carbon atoms of the glucose in question, $C_6H_7O(OH)_5$, thus:

$$2C_6H_7O(OH)_5 = [C_6H_7O(OH)_4]_2O + H_2O;$$

hence cane sugar etc. are octatomic alcohols. In accordance

with this stands the production of oct-acetyl ethers, $C_{12}H_{14}O_3(O.C_2H_3O)_8$, by the action of acetic anhydride.

According to *E. Fischer* (B. **21**, 2631; **22**, 361), lactose and maltose are stereo-isomeric, and possess the constitutional formula:

$$CH_2(OH)—[CH(OH)]_4—CH\begin{cases} O—CH_2 \\ \quad\;\; | \\ O—CH—[CH(OH)]_2—CH(OH)—CHO, \end{cases}$$

in which there is an aldehyde group, and a linking like that in acetal. This is in accordance with the reducing properties of both sugars, their power of yielding hydrazones and of adding on hydrocyanic acid, their alteration by alkalies, and their oxidation to acids containing an atom of oxygen more in the molecule (see below); they may thus be termed *aldehyde sugars*. If, on the other hand, the aldehydic or ketonic group of the hexoses is lost through the formation of complex anhydrides (of this and of the cellulose groups), compounds such as cane sugar are obtained which may be called *anhydride sugars;* these do not reduce, yield no hydrazones, and are more stable with respect to alkalies, etc. Cf. B. **23**, 3060.

Behaviour. 1. For decomposition by mineral acids, *i.e.* hydrolysis, and formation of compound ethers (esters) see above.

2. They form saccharates with bases (see Cane sugar).

Upon the further action of lime, lactose and maltose yield iso-saccharine.

3. Fermentation. Maltose is directly fermentable by yeast, milk sugar only by certain varieties of yeast, and cane sugar not at all until it has been "inverted," which process is effected by the soluble yeast enzyme itself. Milk sugar readily undergoes the lactic fermentation by bacteria.

4. Oxidation converts maltose and lactose in the first instance into malto-bionic and lacto-bionic acids, $C_{12}H_{22}O_{12}$, which are respectively broken up on hydrolysis into *d*-glucose and *d*-gluconic acid, and into galactose and *d*-gluconic acid. Further oxidation gives rise to the same products as are obtained from the glucoses which form their bases.

5. Cane sugar only reduces *Fehling's* solution after inversion, maltose and milk sugar however upon boiling; the last named also reduce an ammoniacal silver solution.

6. Maltose and Lactose yield hydrazones and osazones with phenyl-hydrazine, *e.g.* phenyl-lactosazone (B. **17**, 580); cane sugar, on the other hand, is indifferent towards this reagent until it has been hydrolysed.

Cane sugar or Saccharose, *saccharobiose*, $C_{12}H_{22}O_{11}$. Occurs in red beet (Beta), in the sugar-cane (Saccharum), in the sugar-millet (Sorghum), and in many other plants, chiefly in the stem.

Preparation. (*a*) From sugar-cane by expressing the juice and evaporating it until crystallization begins. (*b*) From sugar-beet by a systematic extraction of the pulp with water, *e.g.* by the "Diffusion process." The impure juice is then treated with lime ("defecation"), the excess of the latter thrown down by carbon dioxide ("carbonatation"), and the syrup filtered through bone-black, and evaporated *in vacuo* to crystallization. From the mother-liquor of molasses, the crystallizable sugar still present can be obtained by combining it with strontia, and decomposing the strontium saccharate by carbon dioxide ("de-sugarizing of molasses"); or by the "Osmose process."

Cane sugar crystallizes in large monoclinic prisms, as is well seen in sugar-candy, and is soluble in one-third of its weight of water. It is not turned brown when heated with potash, and yields saccharates with lime and strontia, *e.g.* $C_{12}H_{22}O_{11} + CaO + 2H_2O$; $C_{12}H_{22}O_{11} + 2CaO$; $C_{12}H_{22}O_{11} + 3CaO$. Concentrated sulphuric acid produces charring (difference from *d*-glucose). Cane sugar melts at 160° and remains in the amorphous condition for some time after cooling (barley-sugar); when heated more strongly, it becomes brown from the formation of caramel or sugar dye, and finally chars. As already mentioned, it readily undergoes inversion.

The percentage of sugar in a solution of unknown strength (p) can be determined from the specific rotatory power ($[\alpha]_D^{20°} = +66 \cdot 5°$), by measuring the angle (α) through which the solution turns the plane of polarization of a ray of polarized light passed through it (cf. p. 38). This is known as Saccharimetry.

Milk sugar or Lactose, *lactobiose*, $C_{12}H_{22}O_{11} + H_2O$, occurs in milk, and only occasionally in the vegetable kingdom. It is obtained by evaporating sweet whey. It crystallizes in hard rhombic prisms, and is much less sweet than cane sugar, and also much less soluble in water. It is converted into "lacto-caramel" at 180°. It shows multi-rotation (p. 315). For its reducing power, see previous page.

Maltose or Malt sugar, *maltobiose*, $C_{12}H_{22}O_{11} + H_2O$, **results** from the action of diastase upon starch during the germination of cereals (preparation of malt). It forms a hard white crystalline mass, very similar to grape sugar, and strongly dextrorotatory. Its power of reducing *Fehling's* solution is only about two-thirds of that of dextrose.

Raffinose or *melitriose*, $C_{18}H_{32}O_{16} + 5H_2O$, is found in the sugar-beet, and therefore in molasses, in the manna of the eucalyptus, and in cotton-seed cake, etc. It is very like cane sugar but tasteless, polarizes very strongly (+), and does not reduce *Fehling's* solution. Upon inversion it yields in the first instance *d*-fructose and "melebiose," the latter then breaking up into galactose and *d*-glucose. For its constitution, see B. **22**, 3118; cf. also A. **232**, 169.

D. The Cellulose Group.

The molecular formula of the members of this series must always be a multiple of the simple analysis-formula $C_6H_{10}O_5$ (or $C_5H_8O_4$?). They are for the most part amorphous and tasteless, insoluble in alcohol and ether, partly soluble in cold water and partly insoluble; thus cellulose is insoluble and also mucilage, the latter merely swelling up with water, while starch forms a jelly with hot water. When boiled with dilute acids or subjected to the action of enzymes, they break up into hexoses or maltose, water being taken up, thus: $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$. The formation of pentoses is frequently to be noticed in this decomposition.

Like the foregoing compounds, therefore, the members of this group are to be regarded as the anhydrides of hexoses or pentoses. Consequently they still possess an alcoholic character and yield acetic and nitric ethers, etc. Most of them are optically active. Dilute nitric acid forms the same oxidation products with them as result from the corresponding hexoses or pentoses, and iodine frequently gives characteristic colourations.

Cellulose, $(C_6H_{10}O_5)_x$, is widely distributed in nature as the **membrane of plant cells; cotton, elder pith, wood, etc., consist of cellulose in a more or less pure state. It can be prepared**

by extracting wadding or Swedish filter paper with caustic potash, hydrochloric acid, water, alcohol and ether successively, or by treating pine wood with sulphuric acid and a little nitric. It forms a white amorphous powder, insoluble in the ordinary reagents but soluble in an ammoniacal solution of cupric oxide, from which it is again thrown down by acids.

When boiled with dilute sulphuric acid, it yields dextrine and *d*-glucose, while the concentrated acid converts it first into **Amyloid**, an amorphous mass which is turned blue by iodine, and finally into dextrine. Parchment paper is simply unglazed paper which has been transformed superficially into amyloid by sulphuric acid. A mixture of nitric and sulphuric acids gives rise to nitric ethers, viz. (according to the intensity of the reaction) either **Gun cotton** or *Pyroxyline*, $C_{12}H_{14}(NO_2)_6O_{10}$, an important explosive, insoluble in alcohol-ether, or **Collodion**, which contains less of the nitric radicle, is not so explosive, and is soluble in alcohol-ether; this latter is used, among other purposes, for making artificial silk. **Celluloid** is produced by treating nitrated cellulose with camphor.

Starch or Amylum, $(C_6H_{10}O_5)_x$, $[C_{36}H_{62}O_{31}?]$, is present in all assimilating plants, being built up in the chlorophyll granules from the carbonic acid absorbed, and is found especially in the nutriment reservoirs of the plants, *e.g.* in the grains of cereals, in perennial roots, potatoes, etc. It is converted into sugar during the transference of the sap. It forms a white velvety hygroscopic powder which consists of round or elongated granules in concentric layers, insoluble in cold water. The interior of these granules consists of "granulose" and their husk probably of cellulose. When they are warmed with water, the latter is broken open and a jelly formed. Both the granules of starch and its jelly are coloured an intense blue by iodine and bright yellow by bromine, from the formation of loose addition compounds. The colour of the iodine starch paste vanishes on heating but reappears on cooling.

When heated with glycerine, the so-called "soluble starch" is formed, also when boiled with water containing sulphuric acid or by the action of diastase. Further treatment with acid converts it into dextrine and *d*-glucose, and with diastase into dextrine and maltose (A. 231, 132). Warming with very little dilute nitric acid to 110° yields dextrine.

Enzymes. As has already been repeatedly mentioned, starch is transformed by the action of diastase into maltose and dextrine. This diastase is an albuminous substance of unknown composition (cf. B. **23**, Ref. 347); it is produced during the germination of barley and other varieties of cereals, is precipitated as a white powder in the aqueous malt extract by alcohol, and causes the conversion of starch into sugar when added to starch paste. The method of its action is as yet unknown. Substances of this nature are termed *enzymes* or, less correctly, *unorganized ferments*, in contradistinction to the *organized ferments*, the micro-organisms (p. 89). Among other enzymes may be mentioned emulsin, which is contained in bitter almonds, the soluble enzyme of yeast, "invertin," the ptyalin of the saliva, the pepsin of the gastric juice, and the trypsin of the pancreas.

The following substances, among others, closely resemble starch:

Lichenin or *moss starch*, present in many lichens, *e.g.* in Iceland moss (Cetraria islandica), which is coloured a dirty blue by iodine; and **Inulin**, present in the roots of the dahlia and many composites (Inula Helenium), which is coloured yellow by iodine and converted into *d*-fructose when boiled with water.

Glycogen or **Animal starch**, *liver starch*, is present *e.g.* in the livers of the mammalia. It is a colourless amorphous powder which is turned wine-red by iodine; after the death of the animal it rapidly changes into *d*-glucose, the same conversion being effected by boiling with dilute acids, while enzymes transform it into maltose.

Gum varieties, $C_6H_{10}O_5$. The gums are amorphous transparent substances widely distributed in the vegetable world, which yield sticky liquids with cold water and are precipitated by alcohol. The gums proper dissolve in cold water to clear solutions, while the mucilages only swell up with water to a liquid which cannot be filtered.

Dextrine or *starch gum*, $C_6H_{10}O_5$, is formed by heating starch either alone or with a little nitric acid, together with *d*-glucose by boiling it with dilute sulphuric acid, and together with maltose by diastase. It exists in various modifications (amylo-dextrine, erythro-dextrine, achroo-dextrine, malto-dextrine), which differ from one another in their behaviour with iodine. It does not reduce *Fehling's* solution even when warmed, and is not directly fermentable by yeast but only after the prolonged action of diastase, maltose being formed. Its applications are numerous.

Dextrine which has been prepared as pure as possible shows a weak aldehydic character, and has been transformed into a closely related alcohol (*Dextrite*) and into a corresponding acid (B. **23**, 3060). Substances similar to dextrine result also from the hexoses by the action of dilute acids upon these ("reverted action"); B. **23**, 2084.

Arabin, $2C_6H_{10}O_5 + H_2O$. Gum arabic or arabin, a clear glassy secretion of many plants, dissolves to a clear solution in water and is much used as a gum. It consists of several amorphous compounds similar to one another, one of which yields *d*-glucose upon hydrolysis and another arabinose; this latter is therefore related to the pentoses.

The same applies to **Wood gum** or *xylane*, since it readily yields xylose. It may be prepared (*e.g.*) from straw or beech wood, by extracting with a solution of caustic soda and precipitating with alcohol and hydrochloric acid.

Bassorin (a mucilage), is the chief constituent of gum tragacanth and gum bassora.

XV. TRANSITION TO THE AROMATIC COMPOUNDS.

In the compounds which have been treated of up to now, a so-called "open carbon chain" has been assumed, *i.e.* one in which the end and middle carbon atoms have to be distinguished from one another. For benzene and its extraordinarily numerous derivatives, on the other hand, it is very probable that six carbon atoms are linked together in a "closed chain," or, in other words, that the two end carbon atoms of the original open chain C—C—C—C—C—C are now joined together. Such a linking is also termed a "ring" (cf. p. 20).

The question, what kinds of closed carbon chains are capable of existence, has therefore of late been the subject of much investigation, and it has been shown that such compounds with three, four, five, and seven carbon atoms can be prepared. The simplest compounds of this nature which are theoretically possible consist of three, four, or five methylene groups, viz., tri-methylene, C_3H_6, tetra-methylene, C_4H_8, and penta-methylene, C_5H_{10}, tetra-methylene being only known in the form of derivatives.

These compounds are also termed "*R*"-*propylene*, "*R*"-*butylene*, and "*R*"-*pentylene* ("R" = ring). Their "official names" are *Cyclo-propane*, *Cyclo-butane*, etc.

A. Tri- Tetra- and Penta-methylenes.

Tri-methylene, C_3H_6. $= H_2C\genfrac{}{}{0pt}{}{\diagup CH_2}{\diagdown CH_2}$ (with the two CH_2 groups joined by a bond), is isomeric with propylene, and results upon heating the so-called tri-methylene bromide, $CH_2Br-CH_2-CH_2Br$, with sodium (*Freund*, J. pr. Ch. (2) **26**, 367). It is a colourless gas, condensible to a liquid at the ordinary temperature under a pressure of 5-6 atmospheres. Unlike propylene it is not attacked by permanganate of potash. It unites with bromine only with difficulty, but more readily with hydriodic acid (*to normal propyl iodide*). *Its heat of combustion is far greater than that of propylene.*—The addition of hydriodic acid or bromine of course effects a "breaking of the ring," *i.e.* the formation of an open chain.

A **Tri-methylene-di-carboxylic acid**, $C_3H_4(CO_2H)_2$, and a **Tetra-methylene-di-carboxylic acid**, $C_4H_6(CO_2H)_2$, have been prepared (at first as ethers) by W. H. Perkin, jun., by the action of ethylene bromide and tri-methylene bromide upon sodio-malonic ether (see B. **17**, 1652, etc., also various papers in Ch. Soc. J.), thus:

$$\begin{matrix}CH_2Br\\ \vdots\\ CH_2Br\end{matrix} + Na_2C\begin{matrix}\diagup CO.OR\\ \diagdown CO.OR\end{matrix} = \begin{matrix}CH_2\diagdown\\ \vdots\\ CH_2\diagup\end{matrix}C\begin{matrix}\diagup CO.OR\\ \diagdown CO.OR\end{matrix} + 2NaBr.$$

The fact that these compounds resist the action of permanganate to a much greater extent than the olefines and the unsaturated acids do is a strong argument in favour of their molecule being "ring-shaped." Further, they only take up bromine with difficulty, and, although combination with hydrobromic acid is more readily effected, that also is relatively difficult. Nascent hydrogen is without action on them.

Penta-methylene, $C_5H_{10} = \begin{matrix}CH_2-CH_2\diagdown\\ \vdots\\ CH_2-CH_2\diagup\end{matrix}CH_2$. On distilling the potassium salt of **Adipic acid**, $\begin{matrix}CH_2\cdot CH_2-CO_2H\\ \vdots\\ CH_2-CH_2-CO_2H\end{matrix}$, there is formed the ketone, **Keto-penta-methylene**, $\begin{matrix}CH_2-CH_2\diagdown\\ \vdots\\ CH_2-CH_2\diagup\end{matrix}CO$, according to the normal reaction. The oxygen in this is replaceable by chlorine, and the latter apparently replaceable by hydrogen with the formation of a liquid boiling at 30°-31°, which is probably penta-methylene itself (*J. Wislicenus*).

Penta-methylene-dicarboxylic acid, $C_5H_8(CO_2H)_2$, has been obtained by means of the malonic ether synthesis (B. 18, 3246).

Leuconic acid, or *penta-keto-pentamethylene*, $C_5O_5 + 4H_2O$, = $CO\langle\begin{matrix}CO-CO\\ \vdots\\ CO-CO\end{matrix}$, and its near relation **Croconic acid**, $C_5O_5H_2$, are derivatives of penta-methylene. Both of these have been prepared from potassium carboxide, a bye-product in the manufacture of potassium, and are highly interesting from a theoretical point of view (*Nietzki* and *Benckiser*, B. **19**, 293; **20**, 1617). See Hex-oxy-benzene.

For Penta-methylene derivatives, cf. also *Fittig*, B. **18**, 3410; *Hantzsch*, B. **20**, 2780; *Zincke*, B. **21**, 2719.

Hepta-methylene, C_7H_{14}. When calcium suberate is subjected to dry distillation, the intra-molecular ketone of suberic acid, **Suberone**, $C_7H_{12}O$, results, and this can be reduced to hepta-methylene (B. **23**, Ref. 282). It is a liquid of a weak benzene odour, which boils at about 100°. The tendency to form a seven-membered ring is however not great, generally speaking (cf. *e.g.* B. **25**, 2898).

Closed chains which contain other polyvalent elements (O, S, N) in addition to carbon are known in considerable number; they must manifestly be assumed, for example, in succinic anhydride, $\begin{matrix}CH_2.CO\\ \vdots\\ CH_2.CO\end{matrix}\rangle O$, in succinimide, $\begin{matrix}CH_2.CO\\ \vdots\\ CH_2.CO\end{matrix}\rangle NH$, in γ-butyro-lactone, $\begin{matrix}CH_2-CH_2-CH_2\\ | \qquad\qquad |\\ O\text{———————}CO\end{matrix}$, in parabanic acid, alloxan, etc., and also in pyridine, quinoline, etc.

At this point must be described three compounds in which closed atomic rings are likewise to be assumed, viz.:

B. Furfurane, C_4H_4O, Thiophene, C_4H_4S, and Pyrrol, $C_4H_4(NH)$.

From these compounds a whole series of derivatives are obtained by the substitution of hydrogen by halogen, and also by the entrance of the groups $-CH_3$, $-CH_2OH$, $-CHO$, $-CO_2H$, etc. In their properties furfurane, thiophene and pyrrol remind one of benzene. Thiophene in particular is delusively like the latter, *e.g.* in odour and boiling point, and its various derivatives often show a marvellous similarity in their chemical and physical relations to the corresponding derivatives of benzene. (See table, below.)

Summary.

Furfurane, C_4H_4O.	*Pyrrol*, $C_4H_4(NH)$.	*Thiophene*, C_4H_4S.	*Benzene*, C_6H_6.
Dibromo-furfurane $C_4H_2Br_2O$.	Tetra-iodo-pyrrol $C_4I_4(NH)$.	Dibromo-thiophene $C_4H_2Br_2S$.	Dichloro-benzene $C_6H_4Cl_2$.
Methyl-furfurane $C_4H_3O(CH_3)$.	α-, β-Methyl-pyrrol $C_4H_3NH(CH_3)$.	α-, β-Methyl-thiophene $C_4H_3S(CH_3)$.	Toluene $C_6H_5(CH_3)$.
Furfurane alcohol $C_4H_3O(CH_2.OH)$.		Thiophene alcohol $C_4H_3S(CH_2.OH)$.	Benzyl alcohol $C_6H_5(CH_2.OH)$.
Furfurol $C_4H_3O(CHO)$.		Thiophene aldehyde $C_4H_3S(CHO)$.	Benzoic aldehyde $C_6H_5(CHO)$.
Pyromucic acid $C_4H_3O(CO_2H)$.	α-, β-Pyrrol-carboxylic acid $C_4H_3NH(CO_2H)$.	α-, β-Thiophene-carboxylic acid $C_4H_3S(CO_2H)$.	Benzoic acid $C_6H_5(CO_2H)$.
Dimethyl-furfurane $C_4H_2O(CH_3)_2$.	α-, β-Dimethyl-pyrrol $C_4H_2NH(CH_3)_2$.	Dimethyl-thiophene $C_4H_2S(CH_3)_2$.	Xylenes $C_6H_4(CH_3)_2$.

Etc.

	n-Methyl-pyrrol $C_4H_4(N.CH_3)$.	Amido-thiophene $C_4H_3S(NH_2)$.	Aniline $C_6H_5(NH_2)$.
		Thiophene-sulphonic acid $C_4H_3S(SO_3H)$.	Benzene-sulphonic acid $C_6H_5(SO_3H)$.

Furfurane, pyrrol and thiophene also resemble one another in many respects. All three boil at relatively low temperatures, (+32°, 131°, 84°), are either insoluble or only slightly soluble in water, but easily in alcohol and ether, and show many analogous colour reactions. Thus pyrrol and thiophene and their derivatives give, for the most part, an intense violet to blue colouration when mixed with isatin and concentrated sulphuric acid, and a cherry-red or violet colouration with phenanthrene-quinone and glacial acetic or sulphuric acid. The vapour of pyrrol colours a pine shaving which has been moistened with hydrochloric acid carmine red (πυῤῥός, fiery-red), while furfurol vapour colours it an emerald green; the latter likewise colours a piece of paper moistened with xylidine- or aniline acetate red. Furfurane is converted by hydrochloric acid, *i.e.* by mineral acids, into an insoluble amorphous powder, and pyrrol into an insoluble amorphous brown-red powder "pyrrol-red" (with evolution of ammonia), while thiophene remains unaltered; the derivatives show a similar behaviour. Pyrrol is distinguished from the two other compounds by having weakly basic properties.

Formation. 1. From mucic acid, $C_4H_4(OH)_4(CO_2H)_2$. This is converted into pyromucic acid (= furfurane-carboxylic acid), $C_4H_3O(CO_2H)$, upon dry distillation, the latter in its turn yielding furfurane when heated with caustic soda. By the action of ammonia, *i.e.* by the dry distillation of the ammonium salt, mucic and pyromucic acids are transformed into pyrrol. Lastly, thiophene-carboxylic acid, and from it thiophene, result upon heating mucic acid with barium sulphide:

$$(a)\ C_4H_4(OH)_4(CO_2H)_2 = C_4H_4O + 2CO_2 + 3H_2O;$$
$$(b)\ C_4H_4(OH)_4(CO_2H)_2 + NH_3 = C_4H_4(NH) + 2CO_2 + 4H_2O;$$
$$(c)\ C_4H_4(OH)_4(CO_2H)_2 + H_2S = C_4H_4S + 2CO_2 + 4H_2O.$$

2. From succinic acid, $C_2H_4(CO_2H)_2$. Succinimide, $C_4H_4O_2(NH)$, yields pyrrol when strongly heated with zinc dust, and sodium succinate yields thiophene when heated with P_2S_3, (*Volhard-Erdmann*, B. 18, 454.)

3. Pyrrol also results from acetylene and ammonia at a red heat, and thiophene when ethylene is led over glowing pyrites.

4. Pyrrol is produced from furfurane when the latter is heated with chloride of zinc and ammonia (B. **20**, Ref. 221).

5. From acetonyl-acetone, $CH_3—CO—CH_2—CH_2—CO—CH_3$, dimethyl-furfurane results with separation of water, dimethyl-pyrrol by heating it with alcoholic ammonia, and finally dimethyl-thiophene with pentasulphide of phosphorus, (*Paal*, B. **18**, 58, 367 ; **20**, 1074.)

This behaviour would indicate that the acetonyl-acetone changes first into the isomeric compound, $CH_3—C(OH)=CH—CH=C(OH)—CH_3$, or $\begin{matrix} CH=C(CH_3)(OH) \\ \dot{C}H=C(CH_3)(OH) \end{matrix}$; upon this assumption the formation of dimethyl-furfurane appears simply as that of an anhydride, that of dimethyl-pyrrol as an exchange of 2(OH) for NH (imide formation), and that of dimethyl-thiophene as the formation of a sulphide, *i.e.* exchange of 2(OH) for S, according to the following equations :

$$\begin{matrix} CH=C(CH_3).OH \\ \dot{C}H=C(CH_3).OH \end{matrix} = \begin{matrix} CH=C(CH_3) \\ \dot{C}H=C(CH_3) \end{matrix}\!\!>O + H_2O.$$

$$NH_3 + \begin{matrix} CH=C(CH_3).OH \\ \dot{C}H=C(CH_3).OH \end{matrix} = \begin{matrix} CH=C(CH_3) \\ \dot{C}H=C(CH_3) \end{matrix}\!\!>NH + 2H_2O.$$

$$H_2S + \begin{matrix} CH=C(CH_3).OH \\ \dot{C}H=C(CH_3).OH \end{matrix} = \begin{matrix} CH=C(CH_3) \\ \dot{C}H=C(CH_3) \end{matrix}\!\!>S + 2H_2O.$$

From the above we have the *constitutional formulæ:*

Furfurane.	Pyrrol.	Thiophene.
$\begin{matrix} CH=CH \\ \dot{C}H=CH \end{matrix}\!\!>O$	$\begin{matrix} CH=CH \\ \dot{C}H=CH \end{matrix}\!\!>NH$ (n)	$\begin{matrix} CH=CH \\ \dot{C}H=CH \end{matrix}\!\!>S.$
(β) (α)	(β) (α)	(β) (α)

These formulæ receive corroboration from the frequently observed fact that those substances are capable of yielding addition compounds with bromine or hydrogen (see Pyrroline). For the constitution of these substances, cf. also p. 334. According to the above formulæ, two isomeric mono-derivatives of furfurane and thiophene are possible: (1) one in which the hydrogen atom (α) which stands nearest to the S, etc., and (2) one in which a quasi-middle hydrogen atom (β) is substituted. As a matter of fact two such isomers have been observed in many cases, *e.g.* two thiophenic acids (see table). These crystallize mixed together, the crystals having a homogeneous appearance although they contain both acids (*V. Meyer*, A. **236**, 200). In the case of pyrrol, on the other hand, three kinds of derivatives (α-, β-, and n-) are both possible and known.

Furfurane, C_4H_4O, is a colourless mobile liquid of chloroform odour which boils at 32°. It is present in pine-wood tar, in the first runnings from ordinary wood tar, etc., and results from the distillation of sugar with lime.

Methyl-furfurane or *sylvane*, $C_4H_3O(CH_3)$, is likewise present in pine-wood tar, and in the products of distillation of sugar with lime. B. Pt. 63°.

Dimethyl-furfurane, $C_4H_2O(CH_3)_2$, results (together with trimethyl-furfurane apparently) like the foregoing compounds from sugar and lime. For its formation from acetonyl-acetone, etc., see p. 328. It is a colourless mobile liquid of a characteristic odour, B. Pt. 94°. Concentrated acids convert it into a resin; it can be retransformed into acetonyl-acetone.

Furfurol, *furfurane aldehyde*, $C_5H_4O_2$ (*Döbereiner*), results from the action of moderately concentrated sulphuric acid upon carbohydrates, particularly arabinose and xylose, from which it is derived by a simple separation of the elements of water:

$$C_5H_{10}O_5 - 3H_2O = C_5H_4O_2;$$

and is also found *e.g.* in fusel oil. It is a colourless oil of agreeable odour which is turned brown by the air; B. Pt. 162°. It has the nature of an aldehyde and shows characteristic reactions (B. **20**, 540).

Methyl-furfurol, $C_5H_3(CH_3)O_2$, is obtained in an analogous manner from the homologue of arabinose, rhamnose, and closely resembles furfurol. It gives a green colouration with alcohol and sulphuric acid. B. Pt. 183°.

Pyromucic acid, $C_5H_4O_3$, $= C_4H_3O(CO_2H)$. Needles or plates of a character similar to that of the crystals of benzoic acid, subliming easily and being readily soluble in hot water and alcohol. M. Pt. 132°. Decolourizes alkaline permanganate almost instantaneously. For its preparation, see A. **261**, 379.

The furfurane derivatives are frequently termed "furane" derivatives for shortness' sake. See "Das Furfuran, etc.," by *A. Bender* (*Gaertner*, Berlin, 1889).

Pyrrol, C_4H_4NH, is a constituent of coal tar (*Runge*) anc bone oil (*Anderson*), and possesses, like many of its homologı a chloroform odour. It is a secondary base. Its imido-hydroჲ is replaceable by alkyl, acetyl or metals. B. Pt. 131°. I formation, see p. 328, and B. 19, 3027.

When pyrrol is acted upon by hydroxylamine the ring is broken, hydrog being taken up and ammonia eliminated, and there is formed the dioxiı of succinic aldehyde, $\begin{matrix} CH_2—CH{=}N.OH \\ CH_2—CH{=}N.OH \end{matrix}$; this latter then yields tetr methylene-diamine upon reduction (B. 22, 1968). Dimethyl-pyrrol passı in a similar manner into acetonyl-acetone dioxime.

Potassium-pyrrol, C_4H_4NK, which is obtained from pyrrol and potassiun or potash, is a colourless compound which is decomposed backwards b) water, and which is converted into pyridine by CH_2I_2 and $NaO(CH_3)$. By the action of iodine and alkali, substitution takes place with the formation of **Tetra-iodo-pyrrol** or **Iodol**, $C_4I_4(NH)$, which crystallizes in yellow plates, and is an antiseptic of milder action than iodoform.

Zinc and glacial acetic acid convert pyrrol into **Pyrroline**, $C_4H_6(NH)$, a colourless liquid and strong secondary base, B. Pt. 91°; and when this latter is heated with hydriodic acid, it is further reduced to **Pyrrolidine**, $C_4H_8(NH)$, a colourless, strongly alkaline base resembling piperidine, and boiling at 85°–88°. This compound is also formed from sodium and succinimide in alcohol. Pyrrolidine yields pyrrolylene, C_4H_6, with methyl iodide and caustic alkali (see Conine; also p. 66). Pyrrolidine is formed synthetically by heating δ-chloro-butylamine (p. 211) with alkali, and by treating ethylene cyanide with sodium and alcohol, thus:

$$\begin{matrix} CH_2—CN \\ CH_2—CN \end{matrix} + 4H_2 = \begin{matrix} CH_2—CH_2.NH_2 \\ CH_2—CH_2.NH_2 \end{matrix} = \begin{matrix} CH_2—CH_2 \\ CH_2—CH_2 \end{matrix}\!\!>\!NH + NH_3;$$

it is consequently designated **Tetra-methylene-imine** (*Ladenburg*, B. 19, 782; 20, 442).

Methyl-pyrrol, $C_4H_3(CH_3)NH$, is found in bone oil in two modifications (α and β), and so is **Dimethyl-pyrrol**, $C_4H_2(CH_3)_2NH$.

Pyrocoll, C_5H_3NO, (yellow plates), the anhydride of **α-Pyrrolıarboxylic acid**, $C_4H_3NH(CO_2H)$, results from the distillation of gelatine. 'he acid itself crystallizes in metallic green prisms, M. Pt. 191°. (Cf. ıble of pyrrol derivatives, also B. 20, 2594.)

Thiophene, C_4H_4S, (*V. Meyer*, B. 16, 1465 etc.), is likewise resent in coal tar, being invariably found i– ·

0·5 p.c.); the same applies to its homologues thiotolene (methyl-thiophene), and thioxene (dimethyl-thiophene), which accompany toluene and xylene, etc. Its boiling point (84°) is almost the same as that of benzene (80·4°), from which it is extracted by repeated shaking up with small quantities of concentrated sulphuric acid, which chiefly dissolves the thiophene (to sulphonic acid). (Cf. B. **17**, 2641, 2852.) It is also attacked more readily than benzene by other reagents such as iodine and bromine.

Thiophene is also obtained synthetically by leading the vapour of ethyl sulphide through a red-hot tube (*Kekulé*), and in small quantity by heating crotonic acid, normal butyric acid, para-aldehyde, erythrite, ether etc. with P_2S_5.

The preparation and properties of the thiophene derivatives are in part almost literally the same as those of benzene. Thus nitric acid acts on thiophene to produce a **Nitrothiophene**, analogous to nitro-benzene, which can in its turn be reduced to amido-thiophene; the latter is, however, much less stable than the corresponding amido-benzene (aniline).

Thiophene-sulphonic acid, $C_4H_3S(SO_3H)$, decomposes into thiophene and sulphuric acid when superheated with water.

Thiotenol, $C_4H_2S(CH_3)(OH)$, the phenol of thiotolene, is formed by heating levulinic acid with P_2S_5, (B. **19**, 553).

The blue colouration which results upon shaking up benzene containing thiophene with isatin and concentrated H_2SO_4, depends on the formation of the blue colouring matter "**Indophenin**," $C_{12}H_7NOS$.

Penthiophene, $CH_2<\begin{smallmatrix}CH=CH\\CH=CH\end{smallmatrix}>S$, would be an analogue of thiophene containing five atoms of carbon. A methyl derivative of it has recently been prepared, which shows exactly the same character and colour reactions as thiophene, but is completely decomposed by $KMnO_4$.

(Cf. *V. Meyer's* "Die Thiophengruppe," Braunschweig, 1888.)

C. Azoles, Pyrazoles, Thiazoles, and related compounds.

1. Pyrazoles.

By the action of phenyl-hydrazine upon aceto-acetic ether, water and alcohol are eliminated, and **Phenyl-methyl-pyrazolone**, $C_{10}H_{10}N_2O$, is formed,—very probably according to the equation:

$$\begin{array}{ccc} CH_3\text{—}CO & & H_2N \\ | & + & | \\ H_2C\text{—}CO.OC_2H_5 & & NH\text{—}C_6H_5 \\ \text{Aceto-acetic ether.} & & \text{Phenyl-hydrazine.} \end{array}$$

$$= \begin{array}{l} CH_3\text{—}C{=}N \\ H_2\dot{C}\text{—}CO \end{array}\!\!>\!N\text{—}C_6H_5 + H_2O + C_2H_5.OH.$$

Phenyl-methyl-pyrazolone.

According to this view it appears as a derivative of:

$$\text{Pyrazole, } \begin{array}{l} HC{=}N \\ H\dot{C}{=}CH \end{array}\!\!>\!NH, = C_3H_4N_2.$$

Pyrazole is theoretically derivable from pyrrol in the same way as pyridine is from benzene, *i.e.* by the exchange of CH for N.

It can be prepared by the action of hydrazine upon epichlorhydrin (B. **23**, 1103), and also from acetylene-dicarboxylic ether and diazo-acetic ether by a complicated reaction (*E. Buchner*, A. **273**, 214). It is a weak base of great stability, crystallizing in colourless needles; M. Pt. 70°, B. Pt. 185°.

Pyrazoline, $C_3H_6N_2$, and **Pyrazolidine**, $C_3H_8N_2$, are derived theoretically from pyrazole by the addition of hydrogen, but only the first of these is as yet known (B. **26**, 408).

By the exchange of two atoms of hydrogen for one of oxygen, the formula of pyrazoline changes into that of:

$$\textbf{Pyrazolone, } \begin{array}{l} HC{=}N \\ H_2\dot{C}\text{—}CO \end{array}\!\!>\!NH \text{ (an oil, B. Pt. 77°; see B. 25, 3441),}$$

and by the entrance of phenyl and methyl into this latter we get:

Phenyl-methyl-pyrazolone (see above). This crystallizes in compact prisms, melts at 127°, and boils without decomposition. As a weak base it dissolves in acids, and as an aceto-acetic ether derivative in alkalies; further, as the latter, it still contains the chemically-active methylene group of this ester. When it is heated with methyl iodide and methyl alcohol it yields:

Phenyl-dimethyl-pyrazolone or Antipyrine, $C_{11}H_{12}N_2O$, which is also produced by the action of aceto-acetic ether upon methyl-phenyl-hydrazine, and which therefore possesses the

constitutional formula, $\begin{matrix} CH_3—C—N(CH_3) \\ \ddot{HC}—CO \end{matrix} > N—C_6H_5$. It crystallizes in white tables or small plates; M. Pt. 113°. The aqueous solution is coloured red by ferric chloride and blue-green by nitrous acid. Antipyrine is an excellent febrifuge. (*L. Knorr*, A. **238**, 137.)

If a solution of antipyrine in toluene is boiled with sodium, and if at the same time a current of carbon dioxide is led through it, hydrogen is taken up and β-**Methyl-amido-croton-anilide** results (B. **25**, 1870).

All the compounds which are constituted similarly to aceto-acetic ether (β-ketonic acids, β-ketonic aldehydes, β-diketones), likewise yield derivatives *of pyrazole with phenyl-hydrazine.*

2. Thiazoles.

Thiazole, C_3H_3NS, = $\begin{matrix} HC—N \\ \ddot{HC}—S \end{matrix} > CH$, is derived from thiophene in the same way as pyridine is from benzene, by the exchange of CH for N, and closely resembles—along with its derivatives—the bases of the pyridine series in properties. It is obtained from amido-thiazole (see below) by exchange of the amidogen group for hydrogen, in a similar manner to the conversion of aniline into benzene. It is a colourless liquid of 117° B. Pt., hardly distinguishable from pyridine; as a base it forms salts, but it is hardly *affected by concentrated sulphuric acid, etc.* (*Hantzsch, Popp*, A. **250**, 273).

Dimethyl-thiazole, $C_3H(CH_3)_2NS$, is produced from monochloro-acetone and aceto-thiamide (p. 199), with elimination of H_2O and HCl, and is exceedingly like α-lutidine (dimethyl-pyridine) in character.

Amido-thiazole, $\begin{matrix} HC—N \\ \ddot{HC}—S \end{matrix} > C—NH_2$, *is formed by the action of mono*-chloraldehyde (p. 149) upon thio-urea, thus:

$$\begin{matrix} CH_2Cl \\ | \\ CHO \end{matrix} + \underbrace{\begin{matrix} HN \\ HS \end{matrix} > C—NH_2}_{\text{Thio-urea (pseudo-form).}} = \begin{matrix} CH—N \\ CH—S \end{matrix} > C—NH_2 + HCl + H_2O.$$

The constitution of the thiazoles follows from this and similar modes of formation. Amido-thiazole is a base of perfect "aromatic" character, like that of aniline. (Cf. *Hantzsch* and his pupils, A. **249**, 1, 7, 31; **250**, 257; **265**, 108.)

3. Imido-azoles; Oxy-azoles.

Compounds analogous to the foregoing are derivable from

Imido-azole, $\begin{matrix} HC—N \\ \ddot{HC}—NH \end{matrix} > CH$ and **Oxy-azole**, $\begin{matrix} HC—N \\ \ddot{HC}—O \end{matrix} > CH$,

which are related to thiazole as pyrrol and furfurane are to thiophene.

Imido-azole, *glyoxaline*, $C_3H_4N_2$, results from the action of concentrated ammonia upon glyoxal, and is a powerful base of weak fish-like odour. It is isomeric with pyrazole. Permanganate of potash oxidizes it, and benzoyl chloride splits it up very readily, *i.e.* "the ring is broken" (B. **25**, 281).

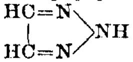
For derivatives, see *Wallach*, A. **184**, 1 ("*Oxalo-ethyline*," etc.); B. **13**, 511; **22**, 568 and 1353.

Alloxan may likewise be regarded as an imido-azole derivative.

For isomers, the *Isoxy-azoles*, cf. (*e.g.*) B. **24**, 130, 857, 3900.

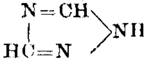
4. Azoles richer in Nitrogen.

Oso-triazole. $C_2H_3N_3$



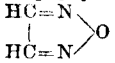
(A. **262**, 314). M. Pt. 22°; B. Pt. 204°. Readily soluble in water. Weakly basic and acid.

Pyrro-diazole. $C_2H_3N_3$



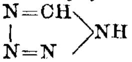
(B. **25**, 225). Needles; M. Pt. 121°. Readily soluble in water.

Furfurazane. $C_2H_2N_2O$



(B. **24**, 1165). (Known as carboxylic acid.)

Tetrazole. CH_2N_4



(B. **25**, 1411). M. Pt. 155°. Readily soluble in water. Is a weak acid; the salts detonate.

The foregoing constitutional formulæ (given in this Class XV.) correspond with their double linkings to *Kekulé's* benzene formula. But formulæ with diagonal (central) linkings have recently been recommended instead of them, these being analogous to the central benzene formula (p. 348). Cf. *Bamberger*, B. **24**, 1758; A. **273**, 373; also A. **249**, 1; **262**, 265; B. **21**, Ref. 888; **24**, 3485, etc.

Class II.—CHEMISTRY OF THE BENZENE DERIVATIVES.

XVI. SUMMARY.

The compounds which have been treated of in Sections I. to XIV. are derivable from the homologous hydrocarbons C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, etc. by the exchange of hydrogen for halogen, hydroxyl or oxygen, amidogen, carboxyl, etc.; and since all the hydrocarbons already mentioned may also be regarded as derivatives of methane (*e.g.* $C_2H_6 = CH_3(CH_3)$ = methyl-methane, $C_3H_8 = CH_2(CH_3)_2$ = dimethyl-methane, $C_2H_4 = CH_2{=}CH_2$ = methylene-methane, $C_2H_2 = CH{\equiv}CH$ = methine-methane, etc.), we may term the compounds which have been described in the foregoing portion of this book *Methane derivatives.*

But in addition to this first class of organic compounds there is a second great class, viz. that of the *Aromatic compounds* or *Benzene derivatives.* The first of these two names is historical but no longer justified by facts, since compounds of agreeable as well as unpleasant odour are to be found in both classes. As benzene derivatives are designated the members of this class which are derivable from the hydrocarbon benzene, C_6H_6 (and also from more complicated hydrocarbons such as anthracene, naphthalene, etc., which are themselves derivatives of benzene), just as the methane derivatives are from methane.

Benzene is, as its formula C_6H_6 shows, a compound much poorer in hydrogen than the paraffins, containing eight H-atoms less than hexane, C_6H_{14}; in the same way all benzene deriva-

tives are much poorer in hydrogen, *i.e.* richer in carbon than the analogous methane derivatives, as is seen by comparing *e.g.* benzoic acid, $C_7H_6O_2$, with heptoic acid, $C_7H_{14}O_2$, or aniline, C_6H_7N, with ethylamine C_2H_7N, etc. etc.

The hydrogen atoms of benzene are, like those of methane, replaceable by the most various elements and atomic groups. By the entrance of halogens, substitution products result, by the entrance of NH_2, aromatic bases, of OH, phenols, of NO_2, nitro-compounds, and of CH_3 etc., the homologues of benzene; there are, in addition to these, aromatic alcohols, aldehydes, acids, etc. Those substituting groups are termed **side chains**.

These benzene derivatives are partly analogous in their properties to the methane derivatives of corresponding composition; in part, however, they show new and peculiar properties of their own, (see pp. 338, 353 *et seq.*). One distinguishes between mono-, di-, tri-, etc. benzene derivatives according as one or two or more hydrogen atoms are replaced by the elements or groups in question; thus, for instance, toluene and chloro-benzene are mono-derivatives, dimethyl-benzene and dichloro-benzene di-derivatives, and so on. Further, just as it was found when speaking of the polyatomic alcohols and acids, that the replacing groups need not be identical, so in this class also innumerable compounds are known containing various substituents. Such compounds have usually some of the characteristics of all those mono-derivatives which result from benzene by the exchange of one H-atom for one of these substituents.

All the derivatives of benzene can be converted either into benzene itself or into very nearly allied compounds by *relatively simple reactions.* Thus all the carboxylic acids of benzene (benzoic, phthalic, mellitic, etc.), yield benzene on distillation with lime, while other acids, such as salicylic, give up CO_2 and yield phenol, and so on; the last-named compound goes into benzene when distilled with zinc dust. The homologues of benzene are converted by oxidation into benzene-carboxylic acids, which give benzene when heated with lime.

The relation of a benzene derivative to its mother substance is therefore a very simple one.

This circumstance is one particularly worthy of note, since the atomic group C_6H_6 is already a tolerably complicated molecule in itself, and also because benzene cannot by any means be transformed into a simpler hydrocarbon containing 5, 4, or 3 C–atoms; when oxidized, which is a matter of difficulty, it goes into carbon dioxide or similar simple organic acids.

Summary of a few Benzene derivatives.

$C_6H_5.CH_3$ Methyl-benzene or toluene.	$C_6H_4(CH_3)_2$ Dimethyl-benzenes or xylenes.	$C_6H_3(CH_3)_3$ Trimethyl-benzenes.
$C_6H_5.Cl$ Chlorobenzene.	$C_6H_4Cl_2$ Dichloro-benzenes.	$C_6H_3Cl_3$ Trichloro-benzenes.
$C_6H_5.OH$ Phenol.	$C_6H_4(OH)_2$ Resorcin, etc.	$C_6H_3(OH)_3$ Pyrogallol, etc.
$C_6H_5.CH_2.OH$ Benzyl alcohol.		
$C_6H_5.NO_2$ Nitrobenzene.	$C_6H_4(NO_2)_2$ Dinitro-benzenes.	$C_6H_3(NO_2)_2OH$ Dinitro-phenols.
$C_6H_5.NH_2$ Aniline.	$C_6H_4(NH_2)_2$ Phenylene diamines.	$C_6H_3(NH_2)_3$ Tri-amido-benzenes.
$C_6H_5.SO_3H$ Benzene-sulphonic acid.	$C_6H_4(NH_2)(SO_3H)$ Sulphanilic acid, etc.	$C_6H_3(SO_3H)_3$ Benzene-tri-sulphonic acid.
C_6H_5—CHO Benzaldehyde.		
$C_6H_5.CO_2H$ Benzoic acid.	$C_6H_4(CO_2H)_2$ Phthalic acids.	$C_6H_3(CO_2H)_3$ Hemi-mellitic acid, etc.
$C_6H_5.CN$ Benzo-nitrile.	$C_6H_4(OH)(CO_2H)$ Salicylic acid, etc.	

The benzene derivatives are connected with one another by the most various reactions. The NO_2–group is readily convertible into NH_2, and the latter is replaceable by halogen, hydrogen and hydroxyl; the halogen is also replaceable by methyl, carboxyl, etc.

Differences between the aromatic and fatty hydrocarbons.

Benzene differs from the fatty hydrocarbons by the following reactions in particular :

1. It forms nitro-benzene with nitric acid :

$$C_6H_6 + HO.NO_2 = C_6H_5.NO_2 + H_2O.$$

2. It yields benzene-sulphonic acid with sulphuric acid :

$$C_6H_6 + HO.SO_3H = C_6H_5(SO_3H) + H_2O.$$

Similarly, almost all the benzene derivatives are capable of forming nitro-compounds and sulphonic acids in nearly theoretical quantity.

As has been already seen, the paraffins are either unaffected by concentrated HNO_3 or H_2SO_4, or only attacked with difficulty, while the olefines form addition products with the latter acid, without separation of water.

3. The homologues of benzene differ from the paraffins especially in their capability of oxidation ; while the latter are only attacked with difficulty by oxidizing agents, the former are readily converted into benzene-carboxylic acids.

4. There are not wanting other distinguishing characteristics between the aromatic hydrocarbons and the paraffins. Thus the halogen compounds C_6H_5X are less active chemically, and the hydroxyl compounds, *e.g.* $C_6H_5(OH)$, are of a more acid nature than the corresponding fatty bodies. The phenyl radicle, C_6H_5, is therefore more acid or "negative" in character than the ethyl, C_2H_5 (cf. *V. Meyer*, B. **20**, 534, 2944; A. **250**, 118).

5. Diazo-compounds are known almost only in the aromatic series, and so on.

Characteristic of the benzene derivatives are their:—

Isomeric relations.

1. While several isomeric mono-derivatives are both theoretically possible and have been practically obtained from each hexane, C_6H_{14}, benzene is only capable of forming a single mono-derivative in each case; isomeric mono-derivatives of benzene are unknown. *The six hydrogen atoms of benzene thus possess an equal value.* This is not merely an empirical law, but one which has been proved experimentally.

Proof of the equal value of the six hydrogen atoms.

Let the six H-atoms be designated as *a*, *b*, *c*, *d*, *e* and *f* respectively.

1. Phenol, $C_6H_5(OH)$, whose hydroxyl may have replaced the H-atom *a*, may be converted into bromo-benzene, C_6H_5Br, and this latter into benzoic acid, $C_6H_5(CO_2H)$. The carboxyl in the latter has therefore also the position *a*, *i.e.* it has replaced the H-atom *a*.

2. The three existing oxy-benzoic acids, $C_6H_4(OH)(CO_2H)$, can either be prepared from benzoic acid or converted into it; their carboxyl therefore has the position *a*, and consequently their hydroxyl must replace some one of the other H-atoms, be it *b*, *c*, or *d*.

3. The oxy-benzoic acids can all give up carbon dioxide, yielding thereby the same phenol, C_6H_5OH, in every one of the three cases:

$$C_6H_4(OH)(CO_2H) = C_6H_5(OH) + CO_2.$$

And since the latter compound contains the hydroxyl in position *a*, according to 1, while the hydroxyl in the oxy-benzoic acids replaces the H-atoms *b*, *c* and *d*, it follows that the hydrogen atoms *a*, *b*, *c* and *d* are of equal value.

4. Now, as will be explained on p. 340, there are present for each H-atom two other pairs of similarly-linked or symmetrical hydrogen atoms, *i.e.* pairs of which either the one or the other may be replaced by any given atomic group, without different substances resulting. But the atoms of such a pair cannot be present in the positions *a*, *b*, *c* and *d*, as in this case three oxy-benzoic acids could not exist. It must therefore be the remaining H-atoms *e* and *f* which are respectively united symmetrically to one of the former, and which are therefore of equal value with them, *i.e.* $e = c$, $f = b$. Since, however, $a = b = c = d$, it follows that all the six hydrogen atoms are of equal value, (*Ladenburg*, B. **7**, 1684.)

2. If two hydrogen atoms in benzene are replaced by other elements or groups, so that di-derivatives result, these latter

must exist in three different isomeric forms. We have thus three di-chloro-benzenes, $C_6H_4Cl_2$, three di-amido-benzenes, $C_6H_4(NH_2)_2$, three di-methyl-benzenes, $C_6H_4(CH_3)_2$, three oxy-benzoic acids, $C_6H_4(OH)(CO_2H)$, and so on. And this is no mere empirical law, for it has been proved that only three isomeric di-derivatives of benzene are capable of existence.

It can be shown that for each H–atom of benzene, *e.g.* for *a*, two pairs of other H–atoms, *e.g.* *b* and *f*, *c* and *e*, are symmetrically linked, so that it makes no difference whether, after *a* is replaced, the second substituent replaces the one or the other of the symmetrically linked hydrogen atoms. According to the above notation, therefore, $ab = af$, and $ac = ae$. On the other hand the combinations *ab* and *ac* are not equivalent but represent isomers; the combination *ad*, the only remaining case, represents the third isomer.

Proofs, that for every H-atom (*a*) two other pairs of symmetrically linked H-atoms exist,

have been advanced by various scientists, especially by *Ladenburg*. One of these may be shortly sketched here.

1. According to *Hübner* and *Petermann* (A. **149**, 129; cf. also Hübner, A. **222**, 67, 166), the (so-called meta-) bromo-benzoic acid, which is obtained by brominating benzoic acid, and whose Br-atom may be in position *c* and CO_2H in position *a*, yields with nitric acid two nitro-bromo-benzoic acids, $C_6H_3Br(NO_2)(CO_2H)$, the NO_2 being (say) in positions *b* and *f*. These are both reduced by nascent hydrogen to the same (so-called ortho-) amido-benzoic acid, $C_6H_4(NH_2)(CO_2H)$, the NO_2 being here changed to NH_2 and the Br replaced by H. Since the same amido-benzoic acid results in both cases, notwithstanding that the nitro groups must be in the place of different H-atoms (say *b* and *f*) from the fact of the two nitro-acids being dissimilar, it follows that *b* and *f* must be linked symmetrically to the H-atom *a*, *i.e.* $ab = af$.

2. In an analogous manner the oxy-benzoic acid (salicylic acid), which can be prepared from the above-mentioned amido-benzoic acid, yields two nitro-derivatives $C_6H_3(OH)(NO_2)(CO_2H)$. If, however, the hydroxyl in these is replaced by hydrogen (a reaction which can be effected by indirect methods), the resulting nitro-benzoic acids, $C_6H_4(NO_2)(CO_2H)$, are identical, and therefore the H-atoms which have been replaced by NO_2 are in a position symmetrical to *a*. When this nitro-benzoic acid is in its turn reduced to amido-benzoic acid,

$C_6H_4(NH_2)(CO_2H)$, it is not the above (ortho-) amido-acid (where $ab=af$) which is obtained, but an isomer. The NO_2-groups cannot therefore here be in the position $b=f$, but must replace two other H-atoms which are likewise symmetric towards *a*, say *c* and *e*, *i.e.* $ac=ae$. (*Hübner*, A. **195**, 4.)

Thus two pairs of H-atoms are symmetrically linked as regards the H-atom *a* : $ab=af$; $ac=ae$. There only now remains the third possible combination *ad*; the sixth H-atom *d* is situated towards the first *a* in a position of its own, *i.e.* in one to which there is no corresponding position.

For further particulars cf. *Ladenburg*, "Theorie der aromat. Verbindungen," Braunschweig, 1876; *Wroblewsky*, A. **168**, 153; **192**, 196; B. **8**, 573; **9**, 1055; **18**, Ref. 148.

It has been assumed in the considerations just detailed that when one compound is converted into another by the exchange of atoms or atomic groups (NH_2 for NO_2, H for OH), this exchange is effected without a so-called "molecular rearrangement" taking place at the same time (see p. 179). Experience has proved that this may be taken for granted in a large number of reactions which proceed with relative smoothness and at comparatively low temperatures. Those instances in which a molecular rearrangement ensues are now well known; especially is this the case in the fusion of sulphonic acids with potash (exchange of SO_3H for OH), a reaction which only takes place at relatively high temperatures, and which frequently leads to isomers of the compounds expected.*

Ortho-, Meta- and Para- Di-derivatives.

Just as the mono-derivatives of benzene can be transformed

* Such a rearrangement of the atoms in the molecule takes place especially at rather high temperatures. Thus, when potassium ortho-oxybenzoate is heated to 220°, the potassium salt of the para-acid results; the three isomeric bromo-benzene-sulphonic acids, $C_6H_4Br(SO_3H)$, and the three bromo-phenols, $C_6H_4Br(OH)$, yield only meta-dioxy-benzene (resorcin) $C_6H_4(OH)_2$, when fused with potash, and not all the three dioxy-benzenes; and ortho-phenol-sulphonic acid, $C_6H_4(OH)SO_3H$, goes into the para-acid when heated, and so on. Reactions of this nature probably arise from the successive taking up and splitting off of atoms or atomic groups, (see crotonic acid, p. 180).

into one another, so from one di-derivative, *e.g.* $C_6H_4(NO_2)_2$, can others, *e.g.* $C_6H_4(NH_2)_2$, be prepared. And since all the di-derivatives of benzene exist in three modifications, they arrange themselves into three great classes, according to their connection with and convertibility into one another. Within each of those three classes the individual members are related by the most various reactions.

In accordance with a proposal made by *Körner* (though upon grounds which are no longer tenable), the above three classes of di-derivatives are termed Ortho-, Meta- and Para-compounds, being written for the sake of shortness with the letters *o*-, *m*-, and *p*-. Thus, *o*-diamido-benzene is that one which results from the reduction of *o*-dinitro-benzene. It can be proved experimentally (p. 345). that the ortho- and meta-positions of the H-atoms are those which occur in the molecule in pairs, while there is no position symmetrical to the para-position. There are likewise experimental data for distinguishing the ortho- and meta-compounds from one another, (see p. 346).

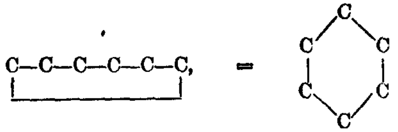
Isomeric Tri- etc. derivatives.

With regard to the tri-derivatives of benzene, $C_6H_3X_3$, there are likewise always three isomers when the three hydrogen atoms are replaced by the same substituent, these being distinguished on theoretical grounds as *v*-, *s*-, and *a*-compounds (p. 345) When, however, only two of the substituents are the same, there are six isomers, and when all three are different, ten. Of tetra-derivatives, $C_6H_2X_4$, with the same substituent, there are likewise three, and of penta- and hexa-derivatives only one; these last three classes may of course be looked upon as di- or mono-derivatives of a completely substituted benzene, or as the latter itself. When the substituents are not the same, many cases of isomerism are known.

Constitution of Benzene; the Benzene Theory.

The views which are at present held as to the constitution of benzene and its derivatives rest principally upon *Kekulé's* benzene theory (1865), which has found almost universal acceptance on account of the elegance with which it explains known facts, (see *Kekulé*, "Lehrbuch der organischen Chemie," II., 493; A. 137, 129). Since its first proposal by him, it has found further support and confirmation from numberless researches. Its chief points are the following:

1. The equal value of the six hydrogen atoms of benzene and the existence of three isomeric di-derivatives would be incomprehensible if an open C–atom chain were ascribed to it, as in the case of the fatty compounds. The requirement that all the H–atoms of benzene shall be linked in a precisely similar manner can, however, be immediately fulfilled if one assumes that the first and last atoms of the six-atom carbon chain are bound together exactly as the remaining atoms are among each other, *i.e.* that the atoms form a "closed chain" or a "ring" (pp. 21 and 55), thus:

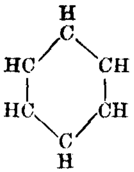


"Benzene ring."

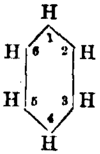
Since, according to this mode of combination, all the C–atoms are similarly grouped, the six H–atoms can also be linked to them symmetrically.

2. The further condition, that the benzene formula which is put forward shall render explicable the existence of three isomeric di-derivatives, is only fulfilled if one C–atom binds one H–atom, *i.e.* if six CH-groups are joined together in ring form.

Leaving aside in the meantime the question as to how the C–atoms are connected by their fourth affinities, we obtain the following graphical formula for benzene:



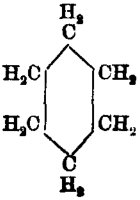
or, more shortly,



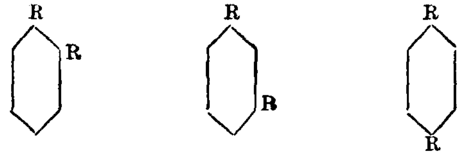
This "hexagon formula" is frequently made use of, on account of the perfect symmetry to which it gives expression.

3. We also arrive in the following manner at the conclusion that the carbon atoms of benzene form a closed chain. Benzene and its derivatives are capable of forming addition compounds, although with far more difficulty for the most part than ethylene, for instance; they can take up two, four or six atoms of hydrogen, chlorine or bromine, according to the conditions of the experiment. Thus benzene, for example, yields hexa-hydro-benzene, C_6H_{12}, upon prolonged treatment with hydriodic acid, and the phthalic acids, $C_6H_4(CO_2H)_2$, yield di-, tetra-, and hexa-hydro-phthalic acids, etc. The resulting hexa-hydro-compounds can not only not combine with any more hydrogen or halogen, etc., but they readily give up the added atoms upon oxidation. Again, benzene hexa-chloride, $C_6H_6Cl_6$, cannot be made to take up more hydrogen or chlorine by any means, but on the contrary it readily yields up 3H and 3Cl. These compounds therefore differ materially from the olefines or their derivatives with which they are isomeric.

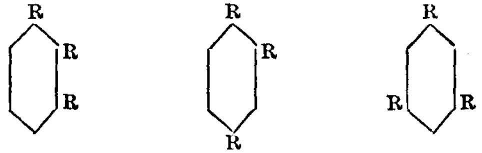
The incapacity of hexa-hydro-benzene to combine with more hydrogen leads unconstrainedly to the following constitutional formula, according to which it appears as hexa-methylene, $(CH_2)_6$, or "R-Hexylene" (*cyclo-hexane*):



4. The above graphical formula for benzene allows of a very simple explanation of the fact that two pairs of symmetrically linked C-atoms (2 and 6, 3 and 5) exist for each C-atom (1), and that one of the modes of combination of two C-atoms (1 and 4) can occur only once in the molecule. The existence of three di-derivatives is also explained very easily thereby, for, according to this formula, only three classes of di-derivatives are possible, viz.: 1. those whose substituents (R) are linked to "neighbouring" C-atoms (1, 2 = 1, 6); 2. those whose substituents are linked to two C-atoms which are "separated" by a third one (1, 3 = 1, 5); and 3. those whose substituents replace "opposite" C-atoms (1, 4). These three varieties of isomers are designated shortly as follows:



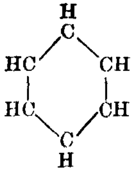
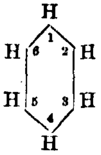
The existence of isomeric tri- etc. derivatives of benzene is likewise readily explained by the above formula; when the substituents, R, are the same, the following cases are possible for tri-derivatives:



In tri-derivatives of the first kind the three substituents are linked to neighbouring or "vicinal" (*v*) carbon atoms, in those of the second to asymmetrically separated (*a*), and in those of the third to symmetrically linked (*s*) C-atoms, and so on.

Characterization of the Ortho-, Meta-, and Para-di-derivatives. Determination of Position.

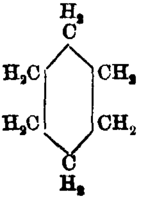
1. The *o*-, *m*-, and *p*-compounds are characterized by their genetic connection within each particular class.

 or, more shortly, 

This "hexagon formula" is frequently made use of, on account of the perfect symmetry to which it gives expression.

3. We also arrive in the following manner at the conclusion that the carbon atoms of benzene form a closed chain. Benzene and its derivatives are capable of forming addition compounds, although with far more difficulty for the most part than ethylene, for instance; they can take up two, four or six atoms of hydrogen, chlorine or bromine, according to the conditions of the experiment. Thus benzene, for example, yields hexa-hydro-benzene, C_6H_{12}, upon prolonged treatment with hydriodic acid, and the phthalic acids, $C_6H_4(CO_2H)_2$, yield di-, tetra-, and hexa-hydro-phthalic acids, etc. The resulting hexa-hydro-compounds can not only not combine with any more hydrogen or halogen, etc., but they readily give up the added atoms upon oxidation. Again, benzene hexa-chloride, $C_6H_6Cl_6$, cannot be made to take up more hydrogen or chlorine by any means, but on the contrary it readily yields up 3H and 3Cl. These compounds therefore differ materially from the olefines or their derivatives with which they are isomeric.

The incapacity of hexa-hydro-benzene to combine with more hydrogen leads unconstrainedly to the following constitutional formula, according to which it appears as hexamethylene, $(CH_2)_6$, or "R-Hexylene" (*cyclo-hexane*):



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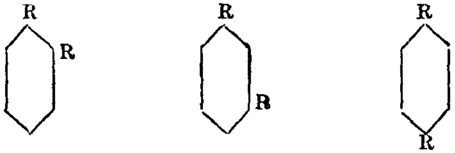
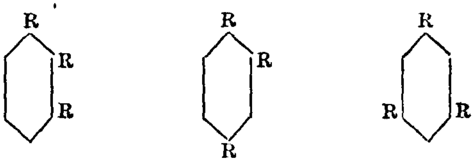


The existence of isomeric tri- etc. derivatives of benzene is likewise readily explained by the above formula; when the substituents, *R*, are the same, the following cases are possible for tri-derivatives:



In tri-derivatives of the first kind the three substituents are linked to neighbouring or "vicinal" (*v*) carbon atoms, in those of the second to asymmetrically separated (*a*), and in those of the third to symmetrically linked (*s*) C–atoms, and so on.

Characterization of the Ortho-, Meta-, and Para-di-derivatives. Determination of Position.

1. The *o*-, *m*-, and *p*-compounds are characterized by their genetic connection within each particular class.

2. The amido-benzoic acid (M. Pt. 145°), which has already been mentioned on p. 340 as resulting from the two nitro- (meta-) bromobenzoic acids, belongs to the class of ortho-compounds, and the amido-benzoic acid (M. Pt. 174°), also mentioned there as prepared from the two nitro- (ortho-) oxy-benzoic acids, to the class of meta-compounds. Consequently the ortho- and the meta-positions are those which are found twice in the molecule, corresponding to the notation used on p. 340: $ab = af$, $ac = ae$. Therefore the third amido-benzoic acid (M. Pt. 187°), which is isomeric with the above two others, is a para-compound, as are likewise all the bi-derivatives which can be prepared from or converted into it by reactions which proceed more or less quantitatively, ("glatt"). The para-di-derivatives are thus characterized as those, the position of whose substituents (*ad*) occurs only once in the benzene molecule.

3. The *o*-, *m*-, and *p*-compounds allow of further characterization experimentally, apart altogether from theoretical considerations. The para-bi-derivatives yield always only one tri-derivative when a third H-atom is replaced by a substituent, the ortho- yield two, while the meta- yield three ($C_6H_3R_3$ or $C_6H_3R_2R'$). It is assumed here that the bi-derivatives contain one and the same substituent.

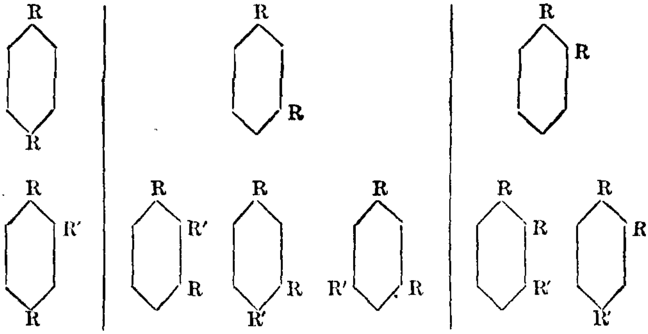
Thus, corresponding to one of the di-bromo-benzenes, $C_6H_4Br_2$, (which is solid, M. Pt. 89°), there is only one tri-bromo-benzene, $C_6H_3Br_3$; corresponding to another (M. Pt. −1°, B. Pt. 224°), there are two; and corresponding to the third (liquid, B. Pt. 219°), three different tri-bromo-benzenes (*Körner*). The same holds for the six nitro-dibromo-benzenes, $C_6H_3Br_2(NO_2)$. The first of the above di-bromo-benzenes is a para-, the second an ortho-, and the third a meta-compound. Precisely analogous relations exist between the three isomeric di-amido-benzenes, $C_6H_4(NH_2)_2$, and the six di-amido-benzoic acids, $C_6H_3(NH_2)_2(CO_2H)$, derivable from them, (*Griess*, B. **7**, 1223); between the three xylenes, $C_6H_4(CH_3)_2$, and the six nitro-xylenes, (*Nölting*, B. **18**, 2687); and between the three phthalic acids, $C_6H_4(CO_2H)_2$, and the six oxy-phthalic acids, $C_6H_3(OH)(CO_2H)_2$. If the bi-derivatives which yield a given equal number of tri-derivatives be tabulated together, it will be found that they belong in every case to one and the same (*o*-, *m*-, *p*-) class, and are therefore convertible into one another.

4. The close agreement between the facts and the theory

with regard to the existence of isomeric di- etc. derivatives has lent a wonderful charm to the endeavour to determine which of the three modes of linking, 1.2 (= 1.6), 1.3 (= 1.5) and 1.4, indicates the ortho-, which the meta-, and which the para-di-derivatives, (" determination of position ").

This point is, in the first instance, easy to solve in the case of the para-compounds. The C-atom 4 holds a position of its own with regard to C-atom 1, *i.e.* there does not exist a C-atom which is linked symmetrically to the position 4, 1; consequently the para-compounds are 1, 4 compounds.

5. Further, it is seen at once from the graphical formula of benzene and from the instances just to be given, that from a 1:4 di-derivative only one, from a 1:2 derivative two, and from a 1:3 derivative three different tri-derivatives are theoretically possible; should the third substituent be different from the two first, these compounds will be all dissimilar, but should it not, then they will be in part identical:



The para-derivatives are therefore to be designated as 1 : 4, the meta- as 1 : 3, and the ortho- as 1 : 2 compounds, (*Körner;* see *Ladenburg's* memoir, already cited).

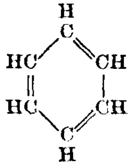
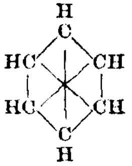
6. Other arguments, which partly forestalled *Körner's* proofs in point of date, have led to the same result. [Cf. *Ladenburg's* proof of the equal value of the three hydrogen atoms of mesitylene, already conjectured by *Baeyer*, *i.e.* of the symmetrical nature of the latter (= 1 : 3 : 5), from which the position 1 : 3 follows for meta-xylene, which can be prepared from it (A. **179**, 163); *Graebe's* arguments with

regard to the constitution 1:2 of ordinary phthalic acid, on account of its formation by the oxidation of naphthalene (A. **149**, 22), etc., etc.].

7. The determination of position of the tri-derivatives depends upon that of the di-derivatives which can be transformed into the former or *vice versa*. If, for instance, both the 1:2 and 1:4 nitro-toluenes, $C_6H_4(CH_3)(NO_2)$, yield one and the same di-nitro-toluene, $C_6H_3(CH_3)(NO_2)_2$, on the introduction of a second nitro-group, the methyl in the latter will be in the ortho-position to one of the nitro-groups and in the para-position to the other, and the compound will therefore be a 1:2:4 or (*a*) compound.

Special Benzene formulae.

The graphical benzene formula which has been employed up to now only disposes, however, of three of the affinities of each carbon atom, and leaves undetermined how the fourth affinity is satisfied. The six carbon atoms having all an equal value, this saturation must be symmetrical. The following conceptions are those mainly to be taken into account with regard to the point:

(I.)  and (II.) 

Kekulé's Benzene formula. *Claus* and *Körner's* Central or Diagonal formula.

Other Benzene formulae:—According to *Dewar*, the carbon atoms 1 and 4 are linked by a single bond, 2 and 3, and 5 and 6 by double ones. According to *Ladenburg*, there are only single bonds between 1 and 4, 2 and 6, and 3 and 5 (prism formula, *Ladenburg*, loc. cit.; A. **172**, 331; B. **23**, 1007. Cf. *Baeyer*, B. **19**, 1797).

Formula (I.) agrees excellently with the modes of formation of benzene and trimethyl-benzene from acetylene and acetone (see below), with its relations to naphthalene (p. 499), and especially with the capability—shown both by benzene and by its derivatives—of forming addition compounds. Combination with H, Cl, etc. thus proceeds here exactly as in the case of ethylene, and a total of six monovalent atoms can be taken up.

It is true that, according to formula (I.), two ortho-biderivatives appear possible, viz. 1, 2 and 1, 6, the two neighbouring carbon atoms being joined together in the first case by a single bond, and in the second by a double

one. As a matter of fact, however, only one ortho-biderivative is known in each case (cf. *Kekulé*, A. **162**, 86).

Recent researches upon the constitution of benzene and its derivatives by *Baeyer* (A. **245**, **251**, **256**, **258**, **269**, 176), and upon similar (and also nitrogen) ring-systems by *Bamberger* (A. **257**, 1), have shown that the nature of the groups entering the benzene molecule is of influence upon the special (fourth) linking of the atoms; so that the constitution of the ring in all benzene derivatives is not to be taken as established without further investigation because a particular formula applicable to benzene itself has been arrived at. On the contrary, *Kekulé's* formula (I.) might suit for certain compounds (as has been proved by *Baeyer* for phloroglucin [B. **24**, 2687]), and formula (II.) for others.

The benzene ring "appears to be capable of existence in two forms, "which are tautomeric, in the sense that each particular deriva- "tive possesses a definite constitution."

Cf. further, *Brühl*, J. pr. Ch. [2] **49**, 201. In this paper he brings forward arguments in favour of *Kekulé's* formula.

In benzene and its carboxylic acids, "para-" or "central-linkings" are probably present, in accordance with formula (II.). The peculiar character of these aromatic compounds, especially their great stability (they are unattacked by a solution of permanganate in soda) may possibly arise from these central bonds, and not from the ring-shape or from the number or nature of the constituents of the ring. And this also applies perhaps to pyridine, thiophene, pyrazole, etc.

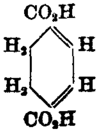
In partially reduced benzene and the carboxylic acids from it, *e.g.* in dihydro- and tetrahydro-terephthalic acids, no para-bonds but only double bonds are present, for these substances possess the same properties as unsaturated compounds with an open chain, being (for example) at once oxidized by alkaline permanganate; and bromine never adds itself on in the para- but always in the ortho-position.

In completely reduced benzene and its carboxylic acids, *e.g.* in hexahydro-terephthalic acid, there are only single carbon bonds, those bodies showing exactly the characters of saturated compounds of the fatty series, and their solutions in soda being unaffected by permanganate.

The benzene ring in C_6H_6 is designated by *Baeyer* as a "tertiary," and that in C_6H_{12}, hexamethylene, as a "secondary" or "reduced" benzene ring.

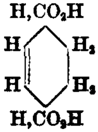
In a partially reduced benzene ring there are therefore, according to the above, still one or two double linkings, *e.g.*:

(I.)



Dihydro-terephthalic acid.

(II.)



Tetrahydro-terephthalic acid.

In order to indicate the position of those double bonds quickly, the plan proposed by *Baeyer* (A. 245, 111) is followed, viz.:—The carbon atoms being numbered 1–6, as given on p. 344, the sign Δ is prefixed to the number of that carbon atom which is linked to the succeeding one by a double bond. The two extended formulae, given above, would thus be expressed:

(I.) = $\Delta^{1,3}$-Dihydro-terephthalic acid.

(II.) = Δ^{6}-Tetrahydro-terephthalic acid.

Laws governing substitution, and influence of the substituents upon one another.

1. A polyvalent element never replaces several hydrogen atoms together in a single benzene nucleus; compounds such as $C_6H_4{=}O$ and $C_6H_3{\equiv}N$ are unknown.

2. In the formation of di-derivatives, etc., several isomers usually result simultaneously, one of them generally in preponderating amount. The position of the new substituents depends upon that of those already present; thus nitro-benzene yields chiefly *m*-nitro-chloro-benzene when chlorinated, and chloro-benzene chiefly *p*-nitro-chloro-benzene when nitrated. As a general rule, when Cl, Br, I, NO_2 and SO_3H enter chloro-, bromo- or iodo-benzene, phenol, $C_6H_5.OH$, aniline, $C_6H_5.NH_2$, or toluene, $C_6H_5.CH_3$, it is always the para-compound which is produced in largest quantity, often together with the ortho-, but only in rare cases with the meta-compound. On the other hand when Cl, Br, I, NO_2 and SO_3H enter into a compound which already contains NO_2–, SO_3H–, or CO_2H–, they almost always take up the meta-position to these latter groups. For a rule to determine whether a given benzene mono-derivative shall give a meta-di-derivative, or a mixture of ortho- and para-di-derivatives, see *Crum Brown* and *Gibson*, Ch. Soc. J., 61, 367.

3. Through the entrance of (negative) nitro-groups or of halogen atoms, the acid character of phenol, *i.e.* the negative nature of phenyl (p. 338), is heightened, while the basic character of amido-compounds is either diminished or entirely done away with. The firm linking of halogen or amidogen

in the benzene nucleus is thereby loosened, so that these substituents become more easily exchangeable, *e.g.* for hydroxyl. (Cf. trinitro-chloro-benzene, trinitro-phenol and tri-nitraniline.)

The intensity of the influence in question is dependent upon the position of the newly entering substituent; thus ortho- and para-chloro- (or bromo-) nitro-benzenes, $C_6H_4Cl(NO_2)$, are transformed into the corresponding nitro-phenols, $C_6H_4(OH)(NO_2)$, when heated with a solution of potash to 120°, and into the corresponding nitranilines, $C_6H_4(NH_2)(NO_2)$, with ammonia at 100°, while meta-chloro- (or bromo-) nitro-benzene does not react at all. In an analogous manner, *o*-dinitro-benzene exchanges a nitro-group for hydroxyl when boiled with caustic soda solution, while the *p*- and *m*-compounds do not.

Further Isomers of the Benzene derivatives.

1. The isomerism of the di-, tri-, etc. derivatives, "isomerism of position" or "nucleus isomerism," has already been treated of on pp. 341 *et seq.*

2. When a substituent enters the benzene nucleus in the first instance and a side chain (p. 336) in the second, the so-called "mixed isomerism" is the result, *e.g.*:

$C_6H_4Cl—CH_3$ and	$C_6H_5—CH_2Cl$;	$C_6H_4(CH_3)_2$ and	$C_6H_5(CH_2.CH_3)$.
Mono-chloro-toluene.	Benzyl chloride.	Xylene.	Ethyl-benzene.

3. When the side chains are isomeric, one speaks of "side chain isomerism," *e.g.*:

$$C_6H_5—CH_2—CH_2—CH_3 \quad \text{and} \quad C_6H_5—CH(CH_3)_2.$$

Normal- and Iso-propyl-benzene.

4. Should the atoms in the side chains (including those chains which are built up from O, S, or N) be unequally divided, "metamerism" in the narrower sense of the word results, *e.g.*:

$$C_6H_4<\genfrac{}{}{0pt}{}{OH}{CO_2.C_2H_5} \qquad \text{and} \qquad C_6H_4<\genfrac{}{}{0pt}{}{O.C_2H_5}{CO_2H}$$

Salicylic ethyl ether. **Ethyl-salicylic acid.**

5. For physical isomerism among the benzene derivatives, *e.g.* the hydro-phthalic acids, see these and also *Baeyer*, A. **251**, 258.

Occurrence of the Benzene derivatives.

Many benzene derivatives occur in nature, *e.g.* oil of bitter almonds, benzoic acid and salicylic acid, while others result from the destructive distillation of organic substances, especially of coal.

The destructive distillation of coal yields (*a*) gases (illuminating gas); (*b*) an aqueous distillate containing ammonium salts etc.; (*c*) tar; and (*d*) coke.

Coal tar contains:

(*a*) Fatty hydrocarbons in small amount.

(*b*) Aromatic hydrocarbons, the most important of which are the following:

Benzene, . . .	C_6H_6	Durene & isom.,	$C_{10}H_{14}$	Fluorene, . .	$C_{13}H_{10}$
Toluene, . . .	C_7H_8	Styrene, . .	C_8H_8	Anthracene, .	$C_{14}H_{10}$
o-, *m*-, and *p*-Xylenes, . .	C_8H_{10}	Naphthalene,	$C_{10}H_8$	Phenanthrene,	$C_{14}H_{10}$
Mesitylene, . .	C_9H_{12}	Di-phenyl, .	$C_{12}H_{10}$	Pyrene, . . .	$C_{16}H_{10}$
Pseudo-cumene,	C_9H_{12}	Acenaphthene,	$C_{12}H_{10}$	Chrysene, . .	$C_{18}H_{12}$

(*c*) Other neutral bodies, *e.g.* alcohol (in very small quantity), benzonitrile, cumarone, C_8H_6O, and carbazole, $C_{12}H_9N$.

(*d*) Phenols, *e.g.*:

Phenol or carbolic acid, C_6H_6O; *o*-, *m*-, and *p*-cresol, C_7H_8O.

(*e*) Bases:

Pyrrol, . . .	C_4H_5N	Aniline, . .	C_6H_7N	Acridine, . .	$C_{13}H_9N$
Pyridine, . .	C_5H_5N	Quinoline, .	C_9H_7N		
and its homologues.		and its homologues.			

(See *Schultz*, "Chemie des Steinkohlentheers," Braunschweig, 1886.)

The presence of the hexahydro-compounds of the hydrocarbons C_6H_6, C_7H_8, C_8H_{10} (*m*- and *p*-), and C_9H_{12} (*s*- and *a*-), and also of other hydrocarbons, has been proved in most natural

petroleums, especially in those from the Caucasus (J. pr. Ch. (2) **45**, 561; cf. p. 54). American petroleum contains, for instance, 0·2 p. c. C_9H_{12}.

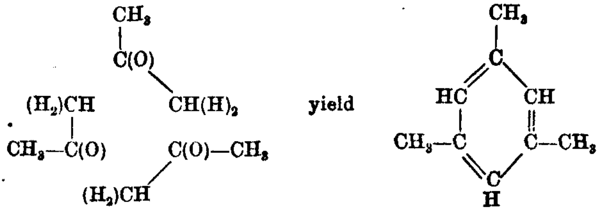
Modes of formation of Benzene derivatives.

The benzene derivatives can only be produced from the fatty compounds by a relatively small number of reactions.

1. Many methane derivatives, *e.g.* alcohol, yield a mixture containing a large number of the derivatives of benzene when their vapours are led through red-hot tubes. Acetylene, C_2H_2, polymerizes at a low red heat to benzene, C_6H_6, (*Berthelot*):

In an analogous manner allylene, C_3H_4, = $CH_3—C\equiv CH$, yields mesitylene, C_9H_{12}, = 1 : 3 : 5 tri-methyl-benzene, $C_6H_3(CH_3)_3$, when distilled with dilute sulphuric acid, while the homologous crotonylene, C_4H_6, yields hexa-methyl-benzene, $C_{12}H_{18}$, = $C_6(CH_3)_6$; brom-acetylene and iod-acetylene polymerize to tri-bromo- and tri-iodo-benzene when exposed to light; propargylic acid, $C_3H_2O_2$, polymerizes to trimesic acid, $C_9H_6O_6$, and so on.

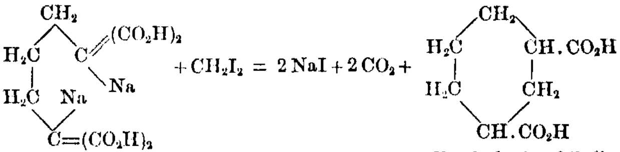
2. Ketones condense to benzene hydrocarbons (p. 155) when distilled with dilute sulphuric acid, *e.g.* acetone yields mesitylene (*Kane*, 1838), and methyl-ethyl-ketone tri-ethyl-benzene, etc.:



3 mols. Acetone. Mesitylene.

3. Certain 1, 2-diketones, aldehyde-acids and ketone-aldehydes are transformed in an analogous manner into benzene derivatives by suitable "condensing" agents; thus, xylo-quinone, $C_6H_2(O_2)(CH_3)_2$, results from the action of alkali upon (2 mols.) di-acetyl, $CH_3—CO—CO—CH_3$ (B. **21**, 1411), and trimesic ether from β-oxy-acrylic ether (B. **20**, 2930).

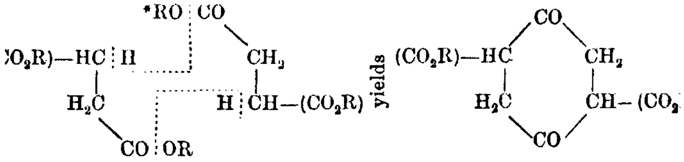
4. By the action of methylene iodide upon the sodium compound of pentane-tetracarboxylic ether, hexahydro-iso-phthalic acid results (*W. H. Perkin, jun.*, Ch. Soc. J., **59**, 798):—



Sodium compound of pentane-tetracarboxylic acid.

Hexahydro-iso-phthalic acid.

5. By acting with sodium upon succino-di-ethyl ether (*Herrmann*, A. **211**, 306; B. **16**, 1411), or upon brom-aceto-acetic ether (*Duisberg*), we obtain the so-called "**succino-succinic ether**" (p. 254), which is a "diketo-hexamethylene-dicarboxylic ether," and is easily convertible into dioxy-terephthalic ether and hydroquinone:



2 mols. Succino-di-ethyl ether.

Succino-succinic ether.

$*R = C_2H_5$.

6. When sodio-malonic ether, $CHNa(CO_2R)_2$, is heated, there is formed Phloroglucin-tricarboxylic ether, which passes into phloroglucin on saponification, the carboxyl groups being broken up.

7. Hexyl iodide, $C_6H_{13}I$, is converted into hexa-chloro-benzene, C_6Cl_6, by heating it with ICl_3, and into hexa-bromo-benzene, C_6Br_6, by bromine at 260°; the latter compound can also be obtained by heating CBr_4 to 300°.

8. **Mellitic acid**, $C_6(CO_2H)_6$, is produced by the oxidation of graphite or lignite by means of $KMnO_4$.

9. **Potassium carboxide**, which is formed by the action of carbonic oxide upon potassium, is the potassium compound of hex-oxy-benzene, $C_6(OH)_6$ (see p. 427).

The converse transformation of Benzene derivatives into Fatty compounds.

1. When the vapour of benzene is passed through a red-hot tube, it is partially decomposed into acetylene.

2. Benzene is oxidized by chloric acid to "**Trichloro-phenomalic acid**," *i.e.* β-trichlor-aceto-acrylic acid, CCl_3—CO—CH=CH—CO_2H (*Kekulé* and *Strecker*, A. **223**, 170).

When chlorine is allowed to act upon phenol in alkaline solution, the benzene ring is broken, and the acids, $C_6H_5Cl_3O_4$, $C_6H_5ClO_4$, etc., are produced (*Hantzsch*, B. **20**, 2780). Pyrocatechin, resorcin, and phloroglucin are also ultimately converted into fatty compounds by treatment with chlorine (B. **25**, 2219). Bromine, acting upon bromanilic acid, yields perbromo-acetone, CBr_3—CO—CBr_3.

3. Nitrous acid (N_2O_3) converts pyrocatechin into dioxytartaric acid (see p. 265), while permanganate of potash, acting upon phenol, gives rise to inactive tartaric acid and oxalic acid (*Döbner*, B. **24**, 1753).

4. Oxidizing agents which are capable of destroying the benzene ring yield carbonic, formic and acetic acids.

5. The hexa-hydro-benzenes are transformed into hydrocarbons of the methane series when treated with hydriodic acid at 280° (*Berthelot*). This decomposition appears, however, to be very difficult of accomplishment.

XVII. BENZENE HYDROCARBONS.

A. Saturated Hydrocarbons.

Summary: [.....] = M. Pt.; (.....) = B. Pt.

C_6H_6	C_6H_6, Benzene (79°).			
C_7H_8	$C_6H_5(CH_3)$, Toluene (110°).			
C_8H_{10}	$C_6H_4(CH_3)_2$, Xylenes (3) *o*-=(142°); *m*-=(137°); *p*-=(137°).	$C_6H_5(CH_2.CH_3)$, Ethyl-benzene (134°).		
C_9H_{12}	$C_6H_3(CH_3)_3$ Trimethyl-benzenes (3). *s* = Mesitylene (163°). *a* = Pseudo-cumene (169°) *v* = Hemellithene (175°).	$C_6H_4(CH_3)(C_2H_5)$ Methyl-ethyl-benzenes (3) Ethyl-toluenes (*e.g.* 162°).	$C_6H_5(C_3H_7)$ Propyl-benzenes 1. Normal-propyl- (157°) 2. Iso-propyl- (= Cumene)(153°).	
$C_{10}H_{14}$	$C_6H_2(CH_3)_4$ Tetra-methyl-benzenes (3): *s* = Durene [79°] (190°). *a* = Iso-durene (195°). *v* = Prehnitene [−4°] (204°).	$C_6H_3(CH_3)_2(C_2H_5)$ Dimethyl-ethyl-benzenes (6 isomers possible).	$C_6H_4(C_2H_5)_2$ Diethyl-benzenes (3) (181° − 184°). $C_6H_4(CH_3)(C_3H_7)$ Cymene (176°) (6 isomers possible).	$C_6H_5(C_4H_9)$ Butyl-benzenes (4 possible) (167° − 180°).
$C_{11}H_{16}$	$C_6H(CH_3)_5$, Penta-methyl-benzene, [51°] (231°); $C_6H_5(C_5H_{11})$, Amyl-benzene, etc.			
$C_{12}H_{18}$	$C_6(CH_3)_6$, Hexa-methyl-benzene, [164°] (264°); $C_6H_3(C_2H_5)_3$, Tri-ethyl-benzene, etc.			
$C_{14}H_{22}$	$C_6H_5(C_8H_{17})$, Octyl-benzene; $C_6H_2(C_2H_5)_4$, Tetr-ethyl-benzene.			
$C_{18}H_{30}$	$C_6(C_2H_5)_6$, Hex-ethyl-benzene [126°] (305°).			

The benzene hydrocarbons are for the most part colourless liquids insoluble in water but readily soluble in alcohol and ether, which distil without decomposition; (durene and penta- and hexa-methyl-benzenes are crystalline). They possess a peculiar and sometimes pleasant ethereal odour, and burn with a very smoky flame. In addition to benzene itself, the presence has been proved in petroleum of its methyl derivative toluene, the three xylenes, the three tri-methyl-benzenes and two tetra-methyl benzenes.

Modes of formation. 1. By treating a mixture of brominated hydrocarbon and iodo- (or bromo-) alkyl with sodium in ethereal solution, (the *Fittig* reaction, A. **131**, 303, analogous to the *Wurtz* reaction, p. 46):

$$C_6H_5Br + CH_3I + 2Na = C_6H_5.CH_3 + NaI + NaBr;$$
$$C_6H_4Br(C_2H_5) + C_2H_5I + 2Na = C_6H_4(C_2H_5)_2 + NaI + NaBr.$$

2. By the action of methyl chloride upon benzene or its homologues in presence of aluminium chloride (*Gustavson*, the so-called "*Friedel* and *Crafts*" reaction), intermediate compounds, such as $Al_2Cl_5(C_6H_5)$, being first formed:

$$C_6H_6 + CH_3Cl = C_6H_5CH_3 + HCl$$
$$C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl, \text{ etc.}$$

This reaction is, like the preceding one, capable of very wide application; by means of it all the hydrogen atoms in benzene can be gradually replaced by methyl.

Zinc and ferric chlorides act in the same way as chloride of aluminium, while ethyl chloride and other haloid compounds, such as chloroform and acid chlorides, may replace methyl chloride. (See respectively triphenyl-methane and the ketones; cf also B. **14**, 2624; B. **16**, 1744; Ann. de chim. et phys. [6] **1**, 419.)

In addition to this synthetical action, aluminium chloride also exerts a "breaking up" or differentiating action on the homologues of benzene, *e.g.* it partly transforms toluene into benzene and xylene, and so on, (B. **17**, 2816; **18**, 338 and 657). Related to the *Friedel-Crafts* reaction is the *Zincke* reaction with zinc dust, (see diphenyl-methane).

Alcohols also, like their haloid ethers, are capable of reacting in an analogous manner in presence of $ZnCl_2$:

$$C_6H_6 + C_4H_9OH = C_6H_5.C_4H_9 + H_2O.$$

3. The benzene hydrocarbons result from their respective carboxylic acids by the splitting off of the carboxyl, *e.g.*, by distillation with soda-lime:

$$C_6H_5CO_2H = C_6H_6 + CO_2;$$
$$C_6H_4(CH_3)CO_2H = C_6H_5.CH_3 + CO_2.$$

4. From sulphonic acids (p. 338) by the separation of the SO_3H-group:

$$C_6H_3(CH_3)_2SO_3H + H_2O = C_6H_4(CH_3)_2 + H_2SO_4.$$

This reaction can be effected by dry distillation, by heating with concentrated hydrochloric acid to 180°, by distillation of the ammonium salt (*Caro*), or by treatment with superheated steam, *e.g.*, in presence of some concentrated sulphuric acid (*Armstrong*, *W. Kelbe*); also by heating with concentrated phosphoric acid (B. **22**, Ref. 577).

5. From the amido-compounds by transforming these into diazo-compounds (p. 394), and boiling the latter with absolute alcohol or with an alkaline stannous solution (B. **22**, 587)

6. By distillation of the phenols (or ketones) with zinc dust.

7. For synthesis, see above. The method of synthesis for paraffins, which was mentioned on p. 47, is also occasionally applicable (see Propyl-benzene).

Isomers and Constitution. The table given on p. 356 shows that the benzene hydrocarbons, from C_8H_{10} on, exist in many isomeric modifications; thus, isomeric with the three xylenes we have ethyl-benzene, with the three tri-methyl-benzenes the three methyl-ethyl-benzenes and the two propyl-benzenes, with durene, cymene, and so on.

The *constitution* of these hydrocarbons follows very simply from their modes of formation. A hydrocarbon $C_{10}H_{14}$ for instance, which is obtained by means of CH_3Cl by the *Friedel-Crafts* reaction, can only be a tetra-methyl-benzene; another of the same empirical formula $C_{10}H_{14}$, which has been prepared from bromo-benzene, butyl bromide and sodium, must be a butyl-benzene; while a third, from *p*-bromo-toluene, normal propyl iodide and sodium, must be a *p*-propyl-toluene (*p*-methyl-N-propyl-benzene), etc. The synthesis therefore determines the constitution.

The (carbon containing) groups CH_3, C_2H_5, etc., which replace hydrogen in benzene, are termed "side chains."

According to the number of side chains it contains, a benzene hydrocarbon is converted by oxidation into a benzene-mono-, di- or tri-, etc., carboxylic acid, *e.g.* benzoic acid, $C_6H_5.CO_2H$, *o*-, *m*-, *p*-phthalic acid, $C_6H_4(CO_2H)_2$, etc. In this way a further means is afforded of determining the constitution of the compounds in question.

If, for example, a hydrocarbon C_9H_{12} yields a benzene-tri-carboxylic acid, $C_6H_3(CO_2H)_3$, upon oxidation, it must contain three side chains, *i.e.*, must be a tri-methyl-benzene; should a phthalic acid on the other hand result, then it can only be an ethyl-toluene. Since cymene yields *p*- (or tere-) phthalic acid, $C_6H_4(CO_2H)_2$, on oxidation, its two side chains must be in the *p*-position towards one another.

The respective isomers resemble each other closely in physical properties, their boiling points—for example—lying very near together. The ortho-derivatives often boil at about 5° and the meta- at about 1° higher than the para-compounds; the boiling point rises with an increasing number of methyl groups. (Cf. p. 33; also B. 19, 2513.)

Behaviour. 1. The benzene hydrocarbons are as a rule easily nitrated and sulphurated, mono-, di- and even tri-derivatives being all usually capable of preparation, according to the conditions. It is only the H-atoms of the benzene nucleus which enter into reaction here, in accordance with the theory which regards the side chains as paraffinic residues, as which they behave. Hexa-methyl-benzene can thus neither be nitrated nor sulphurated.

2. Oxidation. Benzene can only be oxidized with difficulty; permanganate of potash converts it slowly into formic and oxalic acids, some benzoic acid and phthalic acid being produced at the same time. These doubtless result from some previously formed diphenyl.

The homologues of benzene, on the other hand, are readily oxidized to carboxylic acids, the benzene nucleus remaining unaltered, and each side chain—no matter how many carbon atoms it may contain—being converted as a rule into carboxyl.

Nitric acid allows of a successive and often a partial oxidation of individual side chains; chromic acid mixture ($K_2Cr_2O_7 + H_2SO_4$) acts more energetically, converting all the side chains in the *p*- and *m*-

compounds into carboxyl, and completely destroying the *o*-compounds. The latter may be oxidized to the corresponding carboxylic acids by $KMnO_4$.

As is manifest from these two points, the homologues of benzene differ somewhat materially from benzene itself; the H-atoms of the side chains show a different function to those of the benzene nucleus, the former behaving like the hydrogen atoms in a paraffin. It thus follows that toluene and the higher homologues may be derived from methane, etc., by replacement of H by C_6H_5, "phenyl," etc.

$CH_3(C_6H_5)$	$C_3H_7(C_6H_5)$
Toluene or phenyl-methane.	Cumene or phenyl-propane.

3. Reduction. As mentioned on p. 344, benzene and most of its derivatives are capable of taking up six atoms of hydrogen. Benzene itself is only converted into hexa-hydro-benzene, C_6H_{12}, with difficulty, but toluene, xylene and mesitylene combine with hydrogen more easily when they are heated with phosphonium iodide, PH_4I, to a rather high temperature, the compounds $C_7H_8.H_2$, $C_8H_{10}.H_4$ and $C_9H_{12}.H_6$ being formed. The two former can then be made to take up more hydrogen by energetic reaction.

Benzene hexahydride and its analogues, C_nH_{2n}, are colourless liquids insoluble in water, and of somewhat lower boiling point than their mother compounds, into which they can be readily retransformed by oxidation, either by heating with sulphur or by means of fuming nitric acid, nitration also taking place in the latter case. They are found in petroleum, especially in that from the Caucasus (*Beilstein, Kurbatow*). They differ from the isomeric olefines by being insoluble in sulphuric acid, and by not forming addition products with bromine (cf. B. **20**, 1850; A. **234**, 89; B. **21**, Ref. 570).

The partially hydrogenized hydrocarbons, on the other hand, behave more like the olefines; thus, they take up bromine until the point of saturation, C_nH_{2n}, is reached (B. **21**, 836 *et seq.*; cf. also p. 349).

4. Behaviour with halogens. Chlorine and bromine react differently, according to the conditions. In direct sunlight they yield with benzene the addition products $C_6H_6Cl_6$ and $C_6H_6Br_6$, while in diffused daylight, especially in presence of a little iodine, $SbCl_3$ or $MoCl_5$, they give rise to the substitution products C_6H_5Cl, C_6H_5Br, etc. (For further details, and for substitution by iodine, see pp. 70 and 366.)

5. Chromium oxychloride, CrO_2Cl_2, converts the methylated benzene hydrocarbons into aromatic aldehydes (p. 433; cf. B. 23, 1070).

6. The numerous "condensations" which benzene, etc., can undergo with oxygenated compounds in presence of $ZnCl_2$, P_2O_5 or H_2SO_4, and with chlorinated compounds in presence of Al_2Cl_6, are of great interest; thus benzene yields diphenyl-ethane with aldehyde and sulphuric acid, and benzophenone with benzoic acid and phosphorus pentoxide.

6*a*. The methyl-benzenes (but not benzene) "condense" with unsaturated hydrocarbons in a similar manner, in presence of sulphuric acid, *e.g.* xylene with styrene to xylo-phenyl-ethane (*Krämer*, *Spilker*, B. **23**, 3270).

The methyl-benzenes react also with allyl alcohol, by the aid of concentrated sulphuric acid, to form extremely viscous compounds which contain no oxygen. The mineral lubricating oils are probably formed in an analogous manner.

7. In presence of aluminic chloride, oxygen can be introduced into benzene, yielding phenol; sulphur, yielding phenyl sulphide; ethylene, yielding ethyl-benzene; carbon dioxide, yielding benzoic acid; and so on.

By means of carbamic chloride, $CO(NH_2)Cl$, *amides* of the aromatic acids are produced (which see). Being well crystallized compounds, those amides are of much use for the characterization of the hydrocarbons in question (B. **23**, 1190).

The Hydrocarbon C_6H_6.

Benzene, C_6H_6. Discovered by *Faraday* in 1825, and detected in coal tar by *Hofmann* in 1845. Benzene is obtained from the portion of coal tar which boils at 80°–85°, by fractionating or freezing. It may be prepared chemically pure by distilling a mixture of benzoic acid and lime. The ordinary benzene of commerce usually contains thiophene and thus gives the indophenin reaction, but it may be freed from it by repeated shaking up with small quantities of sulphuric acid. M. Pt. 6°; B. Pt. 79°; Sp. Gr. at 0°, 0·9. It burns with a luminous smoky flame, and is a good solvent for resins, fats, iodine, sulphur, phosphorus, etc. When its vapour is led through a red-hot tube, diphenyl is obtained.

Benzene di-hydride ("O.N." *clyco-hexadiene*), $C_6H_6.H_2$. From dibromo-hexa-methylene (which see). A liquid with an odour of leeks; B. Pt. about 81·5°. It is immediately oxidized by permanganate. It yields a crystalline *tetra-bromide* (M. Pt. 181°), and gives a blue colouration with alcoholic sulphuric acid. It is nearly related to the terpenes. (Cf. *Baeyer*, B. **26**, 230.)

Benzene tetra-hydride (*cyclo-hexene*), $C_6H_6.H_4$. From quinitol (*p*-dioxy-hexa-methylene) (which see). B. Pt. about 82°. This compound also has an odour of leeks, and it yields a liquid dibromide.

Benzene hexa-hydride (*cyclo-hexane*), $C_6H_6.H_6$, also termed "*naphthene*," is obtained from the earth-oils of the Caucasus (p. 54), and also synthetically from quinitol. B. Pt. 69°; Sp. Gr. at 0°, 0·75. This compound smells like petroleum. It is stable towards permanganate.

Benzene hexa-chloride, $C_6H_6Cl_6$, is produced by the action of excess of chlorine on benzene in sunlight. It is a solid mass, which is broken up into tri-chloro-benzene and hydrochloric acid on distillation, or when treated with alkalies. Two stereo-isomeric modifications are known.

Benzene hexa-bromide, $C_6H_6Br_6$. M. Pt. 212°.

Mercury di-phenyl, $Hg(C_6H_5)_2$, is an analogue of mercury di-ethyl; it results from the action of mercury upon mono-bromo-benzene. M. Pt. 120°.

The Hydrocarbon C_7H_8.

Toluene, C_7H_8, = $C_6H_5.CH_3$. Discovered in 1837. *Formation:* by the dry distillation of balsam of Tolu and of many resins. Synthesis according to *Fittig* (see above). *Preparation:* from coal tar, in which it is found accompanied by thiotolene. Toluene is very similar to benzene. It boils at 110°, and is still liquid at −28°. CrO_2Cl_2 converts it into benzoic aldehyde, and HNO_3 or CrO_3 into benzoic acid.

Toluene di-hydride, $C_6H_5(H_2).CH_3$, and **-hexa-hydride**, $C_6H_5(H_6).CH_3$, are liquids boiling respectively at 105°–108° and 97°.

Hydrocarbons, C_8H_{10}.

(*a*) *o*-, *m*-, and *p*-**Di-methyl-benzenes** or **Xylenes**, $C_6H_4(CH_3)_2$. The xylene of coal tar consists of a mixture of the three isomers, *m*-xylene being present to the extent of 70 to 85 p.c. These cannot be separated from one another by fractional distillation. *m*-xylene is more slowly oxidized by dilute nitric acid than its isomers, and can thus be obtained with relative ease.

For the separation of those isomers by means of H_2SO_4, see B. **10**, 1010; **14**, 2625; **17**, 444; **25**, Ref. 315; and for their recognition see B. **19**, 2513. Benzene and toluene yield chiefly ortho-, together with a little para-xylene, when subjected to the *Friedel-Crafts* synthesis (B. **14**, 2627).

1. *o*-**Xylene**, which can be prepared synthetically from *o*-bromo-toluene, methyl iodide and sodium, is oxidized to carbonic acid by chromic acid

mixture, and to *o*-toluic acid, $C_6H_4(CH_3)CO_2H$, by dilute nitric acid; it is difficult to nitrate.

2. *m*-**Xylene** or **Iso-xylene** also results from mesitylene, $C_6H_3(CH_3)_3$, 1 : 3 : 5, when this is first oxidized to mesitylenic acid, $C_6H_3(CH_3)_2CO_2H$, and the latter then distilled with lime. Dilute nitric acid only oxidizes it at a temperature of 120°, while chromic acid mixture converts it into iso-phthalic acid, $C_6H_4(CO_2H)_2$. It yields a **Tetra-** and **Hexa-hydride**, $C_8H_{10}.H_4$ and $C_8H_{10}.H_6$; the latter is present in Caucasian petroleum, and boils at 119°.

3. *p*-**Xylene.** Is prepared *e.g.* from *p*-bromo-toluene or, better, *p*-dibromo-benzene, methyl iodide and sodium (B. **10**, 1356; B. **17**, 444). M. Pt. 13°. Dilute nitric acid oxidizes it to *p*-toluic acid, $C_6H_4(CH_3)CO_2H$, and tereph-thalic acid, $C_6H_4(CO_2H)_2$.

The **Di-hydride**, *dihydro-p-xylene*, $C_8H_{10}.H_2$, can be prepared from succino-succinic ester. Liquid; B. Pt. 133°. It has a turpentine odour, and is nearly related to the terpenes. Cf. *Baeyer*, B. **25**, 2122.

(*b*) **Ethylbenzene**, $C_6H_5—C_2H_5$. Results from C_6H_5Br and C_2H_5Br by the *Fittig* reaction; from styrene, $C_6H_5—C_2H_3$ and HI; and from C_6H_6 and C_2H_5Cl by the *Friedel-Crafts* reaction. Is oxidized to benzoic acid. It is found in small quantity in the xylene from tar.

Hydrocarbons, C_9H_{12} (see table).

The most important of these are:

(*a*) **Tri-methyl-benzenes.**

1. **Mesitylene**, 1 : 3 : 5-*tri-methyl-benzene*, $C_6H_3(CH_3)_3$. This is contained in coal tar along with its two other isomeric tri-methyl-benzenes ("tar-cumene"), and can be prepared from acetone or allylene (p. 353). It is a liquid of agreeable odour. Nitric acid oxidizes the side chains one by one, while chromic acid mixture decomposes it completely. It does not form any isomeric substitution products and has therefore a symmetrical constitution, (*Ladenburg*, A. **179**, 160.) B. Pt. 163°.

Mesitylene hexa-hydride, $C_9H_{12}.H_6$, boils at 138°.

2. **Pseudo-cumene**, 1:2:4-*tri-methyl-benzene*. Present in coal tar. It is separated from mesitylene, not by fractional distillation, but by taking advantage of the sparing solubility of pseudo-cumene-sulphonic acid, (B. **9**, 258). Its constitution follows from its formation from bromo-*p*-xylene, 1:4:2, and also from bromo-*m*-xylene, 1:3:4, by the

Fittig reaction. Nitric acid oxidizes the side chains successively. B Pt. 169°.

Hexahydro-ψ-cumene, *nono-naphthene*, C_9H_{18}, is present in Caucasian petroleum. B. Pt. 135°-138°.

3. **Hemellithene**, 1:2:3-*tri-methyl-benzene* (see B. **15**, 1853). Present in coal tar (B. **20**, 903).

(*b*) **Ethyl-toluenes**, $C_6H_4(CH_3)(C_2H_5)$. The *m*- and *p*-compounds are known.

(*c*) **Propyl-benzenes**, $C_6H_5—C_3H_7$. These are oxidized to benzoic acid.

1. **N-Propyl-benzene**, $C_6H_5—CH_2—CH_2—CH_3$, results from bromobenzene and normal propyl iodide by the *Fittig* reaction, and also from benzyl chloride, $C_6H_5.CH_2Cl$, and zinc ethyl.

2. **Iso-propyl-benzene or Cumene**, $C_6H_5—CH{=}(CH_3)_2$, is produced by the distillation of cumic acid, $C_6H_4(C_3H_7)(CO_2H)$, with lime; from benzene and iso- or normal propyl iodide by means of Al_2Cl_6, in the latter case with molecular rearrangement (p. 74); and from benzylidine chloride, $C_6H_5—CHCl_2$, and zinc methyl, this last method furnishing proof of its constitution.

For the transformation of the normal- into the iso-propyl group in cumene and cymene derivatives, see B. **18**, Ref. 152; B. **19**, 2769.

Hydrocarbons, $C_{10}H_{14}$. (See table.)

Among these may be mentioned

Durene, 1:2:4:5- or *s-tetra-methyl-benzene*, $C_6H_2(CH_3)_4$, which has recently been found in coal tar, and can be prepared from toluene and methyl chloride by the *Friedel-Crafts* reaction, or from dibromo-*m*-xylene (from coal tar xylene), methyl iodide and sodium (A. **216**, 200). It is a solid, M. Pt. 79°, and possesses a camphor-like odour. For its constitution, see B. **11**, 31. Both of its isomers are known (see table).

Methyl-propyl-benzenes, $C_6H_4(CH_3)C_3H_7$. The most important of these is *cymene* or *isopropyl-p-methyl-benzene*. It is found in Roman cummin oil (Cuminum cyminum), and results upon heating camphor with P_2S_5 or, better, P_2O_5, also by heating

oil of turpentine with iodine, etc. It has been synthetically built up from *p*-bromo-isopropyl-benzene, methyl iodide and sodium; and also from *p*-bromo-toluene, N-propyl iodide and sodium, the N-propyl- changing here into the iso-propyl group. It is a liquid of agreeable odour, B. Pt. 175°–176°.

Cymene was formerly looked upon as N-propyl-*p*-methyl-benzene (cf. *Widman*, B. **24**, 439). It yields upon oxidation either *p*-toluic, terephthalic, cumic, or oxy-isopropyl-benzoic acid, or *p*-tolyl-methyl-ketone, according to the conditions.

m-**Iso-cymene**, *isopropyl-m-methyl-benzene*, is present in resin oil.

Isomeric with the above are the **Butyl-benzenes**, $C_6H_5(C_4H_9)$, of which three are known, and the **Ethyl-xylenes**.

Cymene di-hydride, $C_{10}H_{14}.H_2$, obtained synthetically from succino-succinic ester, shows exactly the behaviour of the terpenes (B. **26**, 233).

Hydrocarbon, $C_{12}H_{18}$.

Hexa-methyl-benzene, *mellitene*, $C_6(CH_3)_6$, crystallizes in prisms or plates which melt at 164°. It can neither be sulphurated nor nitrated (see p. 359). $KMnO_4$ oxidizes it to mellitic acid, $C_6(CO_2H)_6$.

For the higher homologues see table, p. 356.

B. Unsaturated Benzene Hydrocarbons.

The benzene hydrocarbons containing less hydrogen comport themselves on the one hand like benzene itself, and on the other like the unsaturated hydrocarbons of the fatty series, combining readily with hydrogen, halogen, halogen hydride, etc. They are derived from the olefines or acetylenes by the exchange of H for C_6H_5, thus: $(C_6H_5)CH{=}CH_2$, styrene or phenyl-ethylene; $(C_6H_5)C \equiv CH$, phenyl-acetylene.

Styrene, $C_6H_5.CH{=}CH_2$, occurs along with other compounds in storax (Styrax officinalis), in the juice of the bark of Liquidambar orientale, and in coal tar (being in this last case probably a degradation product of certain acids). It results upon heating cinnamic acid (p. 453) with water to 200°:

$$C_6H_5{-}CH{=}CH{-}CO_2H = C_6H_5{-}CH{=}CH_2 + CO_2.$$

For its preparation see A. **195**, 131. Styrene is a liquid like benzene, and of agreeable odour. B. Pt. 146°. It changes on keeping into the polymeric meta-styrene, an amorphous transparent mass, and goes into ethyl-benzene when heated with hydriodic acid. Addition of HBr converts it into α-bromo-ethyl-benzene, $C_6H_5—CH_2—CH_2Br$. By the condensation of styrene with toluene, in presence of concentrated sulphuric acid, and on subsequent superheating, anthracene results (*Kramer*, *Spilker*, B. **23**, 3169).

Phenyl-acetylene, $C_6H_5.C{\equiv}CH$, is produced, *e.g.* by the separation of CO_2 from phenyl-propiolic acid (p. 455):

$$C_6H_5—C{\equiv}C—CO_2H = C_6H_5—C{\equiv}CH + CO_2.$$

It is a pleasant smelling liquid boiling at 142°, and gives proof of its being an acetylene derivative by yielding white and pale yellow explosive metallic compounds with solutions of silver and cuprous oxides. It combines with water to aceto-phenone, $C_6H_5.CO.CH_3$, when it is dissolved in sulphuric acid and the solution is diluted with water.

XVIII. HALOID SUBSTITUTION PRODUCTS.

Summary.

The numbers in the square brackets [...] indicate melting, and those in the round ones (...) boiling points.

C_6H_5Cl Chloro-benzene (132°). $C_6H_4Cl_2$ Di-chloro-benzenes *o*- : (179°); *m*- : (172°); *p*- : [56°], (173°).	C_6H_5Br Bromo-benzene (156°). $C_6H_4Br_2$ Di-bromo-benzenes *o*- : (224°); *m*- : (219°); *p*- : [89°], (219°).	C_6H_5I Iodo-benzene (185°). $C_6H_4I_2$ Di-iodo-benzenes (*e.g.*, 285°).

$C_6H_3Cl_3$, (3), Tri-chloro-benzenes (208° to 218°).
$C_6H_2Cl_4$, (3), Tetra-chloro-benzenes.
C_6HCl_5, (1), Penta-chloro-benzene.
C_6Cl_6, (1), Hexa-chloro-benzene [226°], (326°).

$C_6H_4Cl(CH_3)$ (3) Chloro-toluenes (156°–160°). $C_6H_3Cl_2(CH_3)$ (6) Di-chloro-toluenes (*e.g.*, 196°). etc.	$C_6H_5—CH_2Cl$ Benzyl chloride (179°). $C_6H_5—CHCl_2$ Benzal chloride (206°). $C_6H_5—CCl_3$ Benzo-tri-chloride (213°).
$C_6H_3Cl(CH_3)_2$, (6) Chloro-xylenes.	$C_6H_4(CH_3)(CH_2Cl)$, Xylyl chlorides.

$C_6H_4(CH_2Br)_2$, (3) Xylylene bromides, etc.,

Haloid substitution products in immense number are derived from the benzene hydrocarbons by the exchange of hydrogen for halogen. They are either colourless mobile liquids or crystalline solids, insoluble in water but readily soluble in alcohol and ether, which distil unchanged, and are distinguished by their peculiar odour and also, in part, by their irritant action upon the mucous membrane. They are heavier than water.

The substitution products of benzene itself and those of its homologues have to be distinguished from one another. In the former the halogen is bound very firmly, far more so than in methyl chloride, ethyl iodide, etc.; it cannot be exchanged for OH (through AgOH), or for NH_2 (through NH_3), etc., sodium almost alone being capable of bringing it into reaction, (see the *Fittig* reaction, p. 357); for an exception, see B. **25**, 1499.

The substitution products of toluene, etc., on the other hand, do not all show a similar behaviour. Some of them, *e.g.*, chloro-toluene, contain the halogen bound very fast, while in others of them, *e.g.*, benzyl chloride, the halogen atoms enter into reaction as readily as do those of the haloid substitution products of the methane series. After oxidation, which transforms all the side chains into carboxyl (p. 359), the halogen remains in the former compounds, with formation of chlorinated, etc., benzoic acids, *e.g.*, $C_6H_4Cl—CO_2H$, but it is eliminated in the latter, benzyl chloride *e.g.* giving benzoic acid, $C_6H_5—CO_2H$. From this it follows that the halogen is present in the one case in the benzene nucleus, and in the other in the side chain.

This is in accordance with the conclusion arrived at on p. 360, of toluene being phenylated methane; chloro-toluene, $C_6H_4Cl.(CH_3)$, is quasi-methylated chloro-benzene and is therefore stable, while benzyl chloride, $C_6H_5—CH_2Cl$, is quasi-phenylated chloro-methyl, and is therefore very active chemically.

The same relations repeat themselves in xylene and the other homologues of toluene, so that it is always easy to arrive at the constitution of a compound from the behaviour of its halogen atoms and from its products of oxidation. Thus a compound $C_7H_6Cl_2$, which yields mono-chloro-benzoic acid upon oxidation, has manifestly the formula $C_6H_4Cl—CH_2Cl$ (chloro-benzyl chloride).

For the capability of reaction of the chlorinated benzenes, cf. also p. 350.

The boiling points of the (position-) isomeric substitution products (*o*-, *m*-, and *p*-compounds), always lie near to one another, and those of the other isomers also are not very far apart from these.

Modes of formation. 1. By the action of chlorine or bromine upon aromatic hydrocarbons there result, according to the conditions, either addition or substitution products, the latter class particularly easily in presence of iodine. (Cf. p. 360, also B. **18**, 607.) Iodine only substitutes directly under the conditions already detailed at p. 70. From benzene all the chlorinated derivatives up to C_6Cl_6 can be obtained in succession, the last named compound resulting with the aid of $MoCl_5$, ICl_3, etc., at a somewhat high temperature. A hexa-bromo-benzene also exists, but not a hexa-iodo-compound. In the case of toluene and its homologues the halogen enters the benzene nucleus alone, if the operation is performed in the cold, with the exclusion of direct sunlight or with the addition of iodine; while, if its vapour is led into the boiling hydrocarbon, or if the experiment is conducted in sunlight and without addition of iodine, it goes almost exclusively into the side chain, (*Beilstein*; *Schramm*; see also B. **13**, 1216).

2. From compounds containing oxygen (the phenols, aromatic alcohols, aldehydes, ketones, and acids), by the action of phosphorus pentachloride or bromide:

$$C_6H_5.OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl.$$

3. From the (nitro- or) primary amido-compounds, these being first converted into diazo-compounds (p. 394). Upon boiling the latter with cuprous chloride or bromide, they are transformed into the corresponding chlorine or bromine compounds, and upon boiling with iodide of potassium, into iodo-substitution products (*Sandmeyer*, B. **17**, 1633, 2650; *Gattermann*, B. **23**, 1218):

$$C_6H_5.N{=}N.Cl = C_6H_5Cl + N_2;$$
$$C_6H_5.N{=}N.Cl + KI = C_6H_5I + N_2 + KCl.$$

The bromine compounds also result upon boiling the diazo-perbromides (p. 398) with absolute alcohol, and the fluorine compounds by a similar reaction, (*Wallach*, A. 235, 255).

3*a*. **By treating the primary hydrazines with iodine and iodide of potassium** (B. **20**, Ref. 552).

4. By heating the haloid-substitution acids with lime:

$$C_6H_4Cl—CO_2H = C_6H_5Cl + CO_2.$$

Mono-chloro-, bromo-, and **iodo-benzene** are colourless liquids of peculiar odour. Their boiling points have been given in the summary.

Di-chloro- and **Di-bromo-benzenes** exist as *o*-, *m*-, and *p*-compounds. The *p*-, and also the *o*-compounds in smaller amount, are obtained directly (see p. 344), while the *m*-compounds are obtained indirectly from *m*-dinitrobenzene according to method 3. The para-compounds are solid and the others liquid.

The significance of the di- and **tri-bromo-benzenes** for the benzene theory has been already indicated at p. 346. The **tri-chloro-benzene** which results by direct substitution has the (asymmetric) constitution 1:2:4. It may also be formed by the separation of 3HCl from $C_6H_6.Cl_6$.

Hexa-chloro- and **-bromo-benzenes** are produced by the thorough chlorination or bromination of benzene, toluene, naphthalene, etc., and also from carbon tetrachloride and bromide, as given at p. 354. They are solid and can be distilled.

p-**Dibromo-benzene hexa-hydride,** *p-dibromo-hexa-methylene*, $C_6H_{10}Br_2$, is obtained from quinitol (which see); it exists in two stereo-isomeric forms.

Iodo-benzene, C_6H_5I, is oxidizable (indirectly) to **Iodoso-benzene,** $C_6H_5.IO$, and this latter to the compound, $C_6H_5.IO_2$, solid explosive substances.

Fluo-benzene, C_6H_5F, is a liquid boiling at 85°; the entrance of fluorine into the benzene molecule thus alters its boiling point only in slight degree.

Mono-chloro- and **-bromo-toluenes,** $C_6H_4Cl(CH_3)$ and $C_6H_4Br(CH_3)$. These mono-substitution products of toluene likewise exist as di-derivatives of benzene in the *o*-, *m*-, and *p*-modifications.

When toluene is chlorinated or brominated, as given on p. 368, the para- and ortho-compounds are formed in approximately equal quantities. *m*-Chloro-toluene is obtained from chloro-*p*-toluidine, $C_6H_3.Cl(NH_2)CH_3$ (from *p*-toluidine and Cl), according to method 3. The *p*-compounds are solid in the cold and the others liquid. Oxidation by HNO_3, CrO_3, or $KMnO_4$ converts them into the haloid-benzoic acids, but chromic acid mixture must only be used in the case of the *p*- and *m*-, and not in that of the *o*-compounds, as it completely disintegrates the latter.

Benzyl chloride, $C_6H_5—CH_2Cl$ (*Cannizzaro*), results upon chlorinating boiling toluene, and benzyl bromide in an analogous manner; the latter can be converted into benzyl iodide by iodide of potassium. The behaviour of these compounds shows them to be the haloid ethers of benzyl alcohol,

C_6H_5—$CH_2.OH$, from which they result by the action of halogen hydride, and into which they are transformed by prolonged boiling with water or, better, with a solution of carbonate of potash. Boiling with potassium acetate yields the acetic ether of this alcohol, with potassium sulph-hydrate the mercaptan, and with ammonia the amine bases.

They are colourless liquids, heavier than water, which boil without decomposition and, like *o*-bromo-toluene, etc., irritate the mucous membrane of the nose and eyes exceedingly. Oxidation converts them into benzoic acid. Benzyl chloride *is used on the large scale for the preparation of oil of bitter* almonds and also of certain dyes.

Benzal chloride, *benzylidene chloride*, C_6H_5—$CHCl_2$, and **Benzo-tri-chloride,** C_6H_5—CCl_3, are produced by the further chlorination of boiling toluene and also by the action of PCl_5 upon the corresponding oxygen compounds, benzoic aldehyde, C_6H_5—CHO, benzoic acid, C_6H_5—CO_2H, and benzoyl chloride, C_6H_5—$COCl$. They are liquids resembling benzyl chloride, and are reconverted into the original oxygen compounds by superheating with water, and into benzoic acid by oxidizing agents. For their relations to cinnamic acid and malachite green, see these.

Chloro-bromo-benzenes, C_6H_4ClBr, **Chlor-iodo-benzenes** and other mixed derivatives also exist in large number.

Substitution compounds of unsaturated hydrocarbons are likewise known, *e.g.* **β-Bromo-styrene,** C_6H_5—$CBr{=}CH_2$, **α-Bromo-styrene,** C_6H_5—$CH{=}CHBr$, etc., etc.

XIX. NITRO-SUBSTITUTION PRODUCTS OF THE AROMATIC HYDROCARBONS.

When benzene derivatives (not merely hydrocarbons) are treated with concentrated nitric acid, most of them are easily dissolved, with evolution of heat, and transformed into nitro-compounds which are precipitated on the addition of water. According to the conditions of the experiment and the nature *of the compound to be nitrated, one or more nitro-groups enter*

the molecule (see *e.g.* phenol). The nitro-groups substitute in the nucleus and only very seldom in the side chain.

Summary.

$C_6H_5(NO_2)$ Nitro-benzene. Liq. B. Pt. 206°.	$C_6H_4(NO_2)_2$ *o*-, *m*-, and *p*-Dinitro-benzenes. Solid. M. Pts. 118°, 90°, and 171°.	$C_6H_3(NO_2)_3$ *s*-Trinitro-benzene. Solid. M. Pt. 121°.
$C_6H_4(CH_3)NO_2$ *o*-, *m*-, *p*-Nitro-toluenes. B.Pts. 218°, 230° and 234° *p*-compound solid.	$C_6H_3(CH_3)_2NO_2$ Nitro-xylenes. *e.g.* 1:3:4, (NO_2 in 4) Liq. B. Pt. 238°.	$C_6H_2(CH_3)_3NO_2$, etc. Nitro-mesitylene. Solid. M. Pt. 42°, B.Pt. 255°.
$C_6H_3(CH_3)(NO_2)_2$ Dinitro-toluenes.	$C_6H_4Cl(NO_2)$ Nitro-chloro-benzenes.	$C_6Br_4(NO_2)_2$ Tetrabromo-dinitro-benzene.
	etc.	

Nitro-compounds are also produced by the action of nitrous acid upon diazo-compounds, in the presence of cuprous oxide, (*Sandmeyer*, B. **20**, 1494):

$$\underbrace{C_6H_5—N{=}N—Cl}_{\text{Diazo-benzene chloride.}} + NHO_2 = \underbrace{C_6H_5—NO_2}_{\text{Nitro-benzene.}} + HCl + N_2.$$

The nitro-compounds are for the most part pale yellow liquids which distil unchanged and volatilize with water vapour, or colourless or pale yellow needles or prisms; sometimes they are also of an intense yellow or red colour. Many of them explode upon being heated. They are heavier than water and insoluble in it, but most of them are readily soluble in alcohol, ether and glacial acetic acid.

The nitro-group in most aromatic nitro-compounds is bound very firmly, as in the case of the nitro-methanes, and is not exchangeable for other groups. Like the latter compounds also, they are easily reduced in acid solution to the corresponding amido-derivatives; in alkaline solution they are converted into azoxy-, azo- and hydrazo-compounds, (see these).

On the other hand, they cannot be prepared according to mode of formation 1 for nitro-methane (p. 111), *i.e.* by the action of $AgNO_3$ on C_6H_5Cl etc.

Nitro-benzene, $C_6H_5(NO_2)$, (*Mitscherlich*, 1834). Results, with evolution of heat, on the gradual addition of benzene to fuming nitric acid, or on treating it with a mixture of sulphuric and the calculated quantity of nitric acid. It is a yellowish liquid with an intense odour of oil of bitter almonds, which solidifies in the cold; M. Pt. + 3°.

Dinitro-benzenes, $C_6H_4(NO_2)_2$. These are produced when benzene is boiled with fuming nitric acid; in this, as in all analogous cases, the two nitro-groups take up the meta-position to one another, very little of the *o*- and *p*-compounds being formed, and, by recrystallizing from alcohol, pure *m*-dinitro-benzene is obtained in long colourless prisms or needles.

The *o*-compound crystallizes in tables and the *p*-compound in needles, both being colourless; they are prepared indirectly by elimination of NH_2 from the corresponding di-nitranilines.

Upon reduction there result first the three nitranilines and then the phenylene-diamines (pp. 386 and 393).

o-Nitro-benzene exchanges a nitro-group for hydroxyl when boiled with caustic soda, and for amidogen when acted on by ammonia, with the formation of *o*-nitro-phenol, $C_6H_4(NO_2)(OH)$ and *o*-nitraniline, $C_6H_4(NO_2)(NH_2)$. The *m*-compound is oxidizable by K_3FeCy_6 to *α*- and *β*-dinitro-phenol.

Nitro-toluenes, $C_6H_4(CH_3)(NO_2)$. When toluene is nitrated, the *p*- and *o*-compounds, with hardly any of the *m*-compound, result. The first is solid, crystallizing in large prisms, and the second liquid, the latter being used as a perfume under the name of "oil of mirbane;" both are employed in the colour industry. *m*-Nitro-toluene can be prepared indirectly from *m*-nitro-*p*-toluidine, $C_6H_3(CH_3)(NO_2)(NH_2)$, by the *Griess* reaction (p. 397).

Further nitration gives rise to:

Dinitro-toluenes, $C_6H_3(CH_3)(NO_2)_2$, of the constitution $CH_3:NO_2:NO_2$ = 1:2:4 and 1:2:6, the two nitro-groups being again in the *m*-position to one another in both cases. (Cf. p. 348.)

Most of these nitro-compounds are of great technical importance, on account of their convertibility into amine bases.

Tri-nitro-tertiary butyl-toluene, $C_6H(CH_3)[C(CH_3)_3](NO_2)_3$, is used as "artificial musk."

Chloro- and **Bromo-nitro-benzenes.**

When chloro- or bromo-benzene is nitrated, *p*-chloro- (or bromo-) nitro-benzenes, and in smaller quantity the *o*-compounds, result. The *m*-compounds must be prepared indirectly by replacing an amido-group in *m*-nitraniline by halogen. The *p*-derivatives have a higher melting point than their isomers, and the *m*-compounds for the most part a higher one than the *o*-derivatives, this law frequently repeating itself in other cases also. The *p*-derivatives are usually also less soluble in alcohol. The *o*- and *p*-compounds, but not the *m*-, exchange halogen for hydroxyl when boiled with potash, and for amidogen when heated with ammonia.

In **Trinitro-chloro-benzene**, $C_6H_2(NO_2)_3Cl$, the chlorine atom has been rendered so easily exchangeable by the acidifying influence of the nitro-groups that the compound behaves as an acid chloride; hence the name "picryl chloride," the chloride of picric acid (p. 350).

Nitro-xylenes, **-mesitylene** and **-pseudo-cumene** are also known in many isomeric modifications, (see table).

We are further acquainted with nitro-derivatives of styrene, viz., *o*-, *m*-, and *p*-**Nitro-styrenes**, $C_6H_4(NO_2)(C_2H_3)$, which can be prepared by indirect methods, and also **α-Nitro-styrene**, $C_6H_5CH{=}CH(NO_2)$, which results directly from the nitration of styrene and contains the nitro-group in the side chain, a necessary consequence of its preparation from benzoic aldehyde and nitro-methane by means of zinc chloride, thus:

$$C_6H_5.CHO + CH_3NO_2 = C_6H_5.CH{=}CH(NO_2) + H_2O.$$

This is one of those relatively rare cases in which the nitro-group enters the side chain upon direct nitration. (Cf. B. **18**, 935, 2438; **19**, 836.)

o-**Nitro-phenyl-acetylene**, $C_6H_4(NO_2)—C{\equiv}CH$, results upon boiling *o*-nitro-phenyl-propiolic acid with water. It crystallizes in colourless needles.

Nitroso-derivatives of the Hydrocarbons.

Nitroso-benzene, $C_6H_5(NO)$, an aromatic compound which contains the nitroso group, NO, in place of a benzene hydrogen atom, is produced by the action of NO.Cl upon mercury di-phenyl dissolved in benzene; it is also obtainable from diazo-benzene. It forms colourless tables, M. Pt. 68°, yields green solutions, and possesses a powerful odour similar to that of cyanic acid. Treated with aniline it gives azo-benzene.

Nitroso-derivatives of tertiary amines result directly by the action of nitrous acid upon the latter. (See Nitroso-dimethyl-aniline, $C_6H_4(NO)N(CH_3)_2$, p. 388.)

XX. AMIDO-DERIVATIVES OF THE BENZENE HYDROCARBONS.

(See table, p. 375.)

Aniline, the simplest of the aromatic bases, may be regarded (1) as benzene in which a hydrogen atom is replaced by amidogen, ("amido-benzene"), or (2) as ammonia in which a hydrogen atom is replaced by phenyl, C_6H_5—, ("phenyl-amine"). According to the former view, amido-compounds are derived from all the benzene hydrocarbons, and not only monamines (containing NH_2), but also di-amines ($2NH_2$), tri-amines, etc.; according to the latter, the phenyl group *may enter anew with the formation of secondary or tertiary* amines. Secondary and tertiary amines, and even quaternary ammonium compounds may also result from the entrance of alcohol radicles into the above monamines, diamines, etc.

NH_2, etc., may likewise substitute in the side chain.

An extraordinarily large number of aromatic bases are thus theoretically possible and also actually known (see table). They closely resemble in some ways the nitrogen bases of the alcohol radicles, form salts with acids—frequently with evolution of heat—and double salts with chloride of platinum, possess a basic odour, give rise to white clouds with volatile acids, and distil for the most part unchanged, etc. Speaking *generally, however, they are weaker bases than the alcoholic* amines, since the phenyl group, C_6H_5, possesses a negative character, and not—like the alcohol radicles—a positive; thus the salts of diphenylamine are decomposed even by water, and triphenylamine no longer possesses basic properties, while dimethyl-aniline has a strongly marked basic character.

[*Continued on p.* 376.

Summary.

	Primary.	Secondary.	Tertiary.
MONAMINES.	$C_6H_5.NH_2$ **Aniline** [−8°] (183°).	$(C_6H_5)_2NH$ **Diphenylamine** [54°] (302°).	$(C_6H_5)_3N$ **Triphenylamine** [127°].
	$C_6H_4(CH_3)NH_2$ **Toluidines.** o-: m-: p-: (199°), (200°), [45°] (198°).	*Alkylated Bases.* $C_6H_5.NH.CH_3$ Methyl-aniline (192°).	$C_6H_5.N(CH_3)_2$ **Dimethyl-aniline** (192
	$C_6H_3(CH_3)_2NH_2$ (6) Xylidines, (*e.g.* 217°).	$C_6H_5.NH.C_2H_5$ Ethyl-aniline (204°).	$C_6H_5.N(C_2H_5)_2$ Diethyl-aniline (213°
	$C_6H_2(CH_3)_3NH_2$ Pseudo-cumidine [62°]. —	*Nitrosamines.* $(C_6H_5)_2N.NO$ Nitroso-diphenylamine [66°]	*Nitroso-derivatives.* $C_6H_4(NO).N(CH_3)_2$ Nitroso-dimethyl-anili [85°]
	$C_6H_4(NO_2)NH_2$ Nitranilines, o-: m-: p-: [71°] [114°] (285°) [147°]. —	*Acid Derivatives.* $C_6H_5.NH(C_2H_3O)$ **Acetanilide** [114°].	$C_6H_5.N(CH_3)(C_2H_3O$ Methyl-acetanilide [9
	$C_6H_5(CH_2.NH_2)$ Benzylamine (183°).	$CO.(NHC_6H_5)_2$ Carbanilide [235°].	$CO(N.C_6H_5)$ Phenyl cyanate (163°
	$C_6H_5(CH_2.CH_2.NH_2)$ Phenyl-ethylamine (193°), etc.	$CS(NHC_6H_5)(NH_2)$ Phenyl-thio-urea [154°] etc.	$CS(N.C_6H_5)$ Phenyl-isothiocyanat (222°) etc.
DIAMINES, etc.	$C_6H_4(NH_2)_2$ Phenylene-diamines, o-: [102°] (252°) m-: [63°] (287°) p-: [147°] (267°).	$C_6H_4(NH_2)[N(CH_3)_2]$ **Amido-dimethyl-aniline** p-: [41°] (257°).	
	$C_6H_3(CH_3)(NH_2)_2$ Toluylene-diamines *e.g.* 1 : 2 : 4 [99°] (286°).	$C_6H_4(NH_2)(NH.C_6H_5)$ Amido-diphenylamine p-: [66°].	
		$NH<\begin{matrix}C_6H_4.NH_2\\C_6H_4.NH_2\end{matrix}$ *p*-Diamido-diphenylamine [15	
	$C_6H_3(NH_2)_3$ **Triamido-benzenes.**		
	$C_6H_2(NH_2)_4$ **Tetramido-benzene.**	$NH[C_6H_4.N(CH_3)_2]_2$ *p*-**Tetramethyl-diamido-diphenylamine.**	

The diamines have a more strongly basic character than the monamines and are more readily soluble in water.

A. Primary Monamines.

Isomers. The isomerism of the aromatic is in part analogous to that of the fatty amines (p. 123), *e.g.*, dimethyl-aniline is isomeric with the methyl-toluidines and the xylidines. Cases of isomerism are also caused by the amido-group being present in the benzene nucleus in the one case and in the side chain in the other. Finally all the isomeric relations of the aromatic hydrocarbons (bi-derivatives, etc.) may also come into play here.

Constitution. As already seen at pp. 124 *et seq.*, amines are very easy to characterize as primary, secondary, etc. Not only their modes of formation but also their behaviour shows whether the amido-group is present in the benzene nucleus or in the side chain.

Modes of formation. 1. The most important mode of preparation of the primary aromatic bases, and also of the di-amines, etc., consists in the reduction of the nitro-compounds:

$$\underbrace{C_6H_5.NO_2}_{\text{Nitro-benzene.}} + 3H_2 = 2H_2O + \underbrace{C_6H_5.NH_2}_{\text{Aniline.}}$$

$$\underbrace{C_6H_4(NO_2)_2}_{\text{Di-nitro-benzenes.}} + 6H_2 = 4H_2O + \underbrace{C_6H_4(NH_2)_2}_{\text{Phenylene-diamines.}}$$

The reduction of nitro- to amido-compounds goes on especially well in an acid solution, *e.g.*, by the gradual addition of the former to a warm mixture of tin or stannous chloride and hydrochloric acid. On a manufacturing scale iron and a limited amount of hydrochloric acid are used (*Béchamp*), also frequently zinc dust and hydrochloric or acetic acid. Ammonium sulphide (*Zinin*), ferrous sulphate and baryta water, etc., also effect the reduction.

Sulphide of ammonium acts more mildly than tin and hydrochloric acid and is therefore of special value for the partial reduction of dinitro-compounds (*see* nitraniline). An alcoholic solution of stannous chloride containing hydrochloric acid may also be used for this purpose, (B. **19**, 2161).

Amines also result from the reduction of nitroso-compounds, (see nitroso-dimethyl-aniline.)

2. By heating phenols with the compound of zinc chloride and ammonia, or of calcium chloride and ammonia, to 300° (*Merz*), secondary amines being formed at the same time:

$$C_6H_5.OH + HNH_2 = C_6H_5.NH_2 + H_2O.$$

This reaction goes on more easily in the presence of negative groups, *e.g.* with the nitro-phenols, (B. **19**, 1749).

3. By distilling amido-acids with lime, sometimes by merely heating them alone:

$$C_6H_4(NH_2)CO_2H = C_6H_5.NH_2 + CO_2.$$

4. By heating secondary and tertiary bases (such as mono- and dimethyl-aniline), which have been formed by the introduction of the alcohol radicle into primary aromatic bases, with strong hydrochloric acid to 180°, the alcoholic radicle can be eliminated again in the form of alkyl chloride with reproduction of the primary bases:

$$C_6H_5.N(CH_3)_2 + 2HCl = C_6H_5.NH_2 + 2CH_3Cl.$$

If the temperature is raised higher, the separated CH_3Cl (*i.e.* chloro-alkyl) acts further upon the primary amine, causing the replacement of hydrogen of the benzene nucleus by alcoholic radicle and the consequent formation of primary bases which are homologous with the original amine; in this way toluidine hydrochloride results upon heating hydrochloride of methyl-aniline to 335°:

$$C_6H_5.NH(CH_3), HCl = C_6H_5.NH_2 + CH_3Cl = C_6H_4(CH_3)NH_2, HCl.$$

The methyl groups which thus enter the nucleus take up the *o*- or *p*-, and not the *m*-position, to the regenerated NH_2.

In an analogous manner one finally obtains from trimethyl-phenyl-ammonium iodide, $C_6H_5.N(CH_3)_3I$, mesidine hydriodide, $C_6H_2(CH_3)_3.NH_2$, HI. Hydrochloride of diphenylamine does not show this reaction.

4ᵃ. The formation of (*e.g.*) amido-isobutyl-benzene, by heating aniline hydrochloride with isobutyl alcohol to 250°, depends upon the same principle, thus:

$$C_6H_5.NH_2, HCl + C_4H_9OH = C_6H_4(C_4H_9).NH_2, HCl + H_2O.$$

5. For the formation of amido-compounds from nitro-haloid-benzenes or *o*-dinitro-benzenes, see p. 373.

6. By heating the potassium salts of sulphonic acids with sodio-amide, $NaNH_2$, (B. **19**, 902).

7. The aromatic amines cannot be obtained by heating chloro-benzene, etc. with ammonia (see p. 367). Benzylamine, however, and all analogously constituted bases, which contain

the NH_2-group in the side chain, result by the methods which apply in the preparation of amines of the fatty series. Thus benzylamine is formed by the action of ammonia or, better, of acetamide upon benzyl chloride (the latter method giving rise, of course, to the readily saponifiable acetyl-benzylamine), by reduction of benzaldehyde-phenyl-hydrazone (p. 434; B. 19, 1924), etc. The above also holds good for secondary and tertiary bases of this kind.

Properties. The primary monamines are partly liquid, partly solid and beautifully crystallizing bases. They are colourless when pure, but readily become brown when exposed to the air, and possess a weakly basic and not disagreeable odour. Aniline is somewhat soluble in water (1 : 31), its homologues less so.

Behaviour. 1. Most of them yield with acids salts which crystallize well and which are usually readily soluble in water. They do not however unite with very weak acids, such as carbonic, and they are therefore separated from their salts in the free state by sodium carbonate. Sodium acetate often acts in the same way (when no acetates exist). They yield double compounds with many metallic salts, especially with platinic chloride [*e.g.* $2(C_6H_7N,HCl) + PtCl_4$], and with gold chloride; also with stannous and zinc chlorides, etc. The platinum double salts are often sparingly soluble and therefore suited for the isolation of the bases.

Besides these there exist the so-called addition salts of those bases, *e.g.* aniline zinc chloride, $2C_6H_7N + ZnCl_2$, aniline mercuric chloride, $2C_6H_7N + HgCl_2$, and so on.

2. When aniline is heated with potassium or sodium, the hydrogen is replaced by metal with formation of the compounds C_6H_5NHK and $C_6H_5NK_2$. These yield di- and triphenylamine with bromo-benzene, and decompose immediately with water.

3. For behaviour with sulphuric and nitric acids and with halogens, see pp. 410 and 386.

4. The primary aromatic bases are analogous in every respect to the primary fatty ones, methyl iodide, benzyl chloride etc. transforming them into secondary, tertiary and quaternary compounds:

$$C_6H_5.NH_2 + CH_3I = C_6H_5.NH(CH_3), HI;$$
$$C_6H_5.NH(CH_3) + CH_3I = C_6H_5.N(CH_3)_2, HI;$$
$$C_6H_5.N(CH_3)_2 + CH_3I = C_6H_5.N(CH_3)_3I.$$

The secondary and tertiary bases can be liberated from their hydriodides by soda, but moist oxide of silver must be used in the case of the ammonium bases, (see p. 125).

5. Aldehydes react with the primary bases, with elimination of water, thus:

$$CH_3.CHO + 2C_6H_5.NH_2 = \underbrace{CH_3.CH(NH.C_6H_5)_2}_{\text{Ethylidene-diphenyl-diamine.}} + H_2O.$$

Benzoic aldehyde, however, reacts as follows:

$$C_6H_5.CHO + NH_2.C_6H_5 = \underbrace{C_6H_5.CH{=}N{-}C_6H_5}_{\text{Benzylidine-aniline.}} + H_2O.$$

Condensation products of this latter kind can also be obtained with the fatty aldehydes, but they polymerize readily (*v. Miller, Plöchl*, B. **25**, 2020).

6. Just as acids yield amides with ammonia, so are they capable of forming "anilides" with aniline, etc., *e.g.* acetic acid and aniline give acetanilide:

$$C_6H_5.NH_2 + C_2H_3O.OH = C_6H_5.NH(C_2H_3O) + H_2O.$$

These anilides may either be looked upon as acetylated etc. amines or as phenylated etc. amides, the formula $C_2H_3O.NH(C_6H_5)$ corresponding with the latter view. They are in every respect analogous in their chemical behaviour to the ordinary amides, especially to the alkylated amides (p. 194), being broken up again into their components by alkalies, and being formed by analogous methods, *e.g.* by heating the acid or, better, its anhydride or chloride with the amine in question, thus:

$$\underbrace{C_6H_4(CH_3)NH_2}_{\text{Toluidine.}} + CH_3.COCl = \underbrace{C_6H_4(CH_3).NH.C_2H_3O}_{\text{Acet-toluide.}} + HCl.$$

7. When warmed with chloroform and alcoholic potash, the primary bases, like those of the fatty series, yield iso-nitriles of stupefying odour. When they are warmed with carbon bisulphide thio-ureas result, and from the latter iso-thiocyanates, *e.g.* on treatment with phosphoric acid, (cf. pp. 124 and 297).

8. Nitrous acid converts the primary aromatic amines in acid solution into diazo-compounds (p. 394), and in the absence of acids into diazo-amido-compounds (p. 398). The diazo-compounds go into phenols when boiled with water, so that NH_2 is here indirectly exchangeable for OH, as is the case directly with the amines of the fatty series. When the amines are warmed with ethyl nitrite in alcoholic solution, the amido-group is eliminated, *i.e.* replaced by hydrogen (p. 396).

9. The oxidation products of the primary bases are very various, phenols, quinones, azo-compounds, aniline black, etc., resulting according to the conditions; a mixture of aniline and toluidine yields magenta (fuchsine).

10. The bases which contain the amide in the side chain possess, in contradistinction to the purely aromatic amines, the character of the amines of the fatty series. They are thus *e.g.* not convertible into diazo-compounds.

B. Secondary Monamines.

We have to distinguish here between purely aromatic secondary amines, such as diphenylamine, and mixed secondary bases which contain an aromatic residue and a radicle of the fatty series.

Modes of formation. 1. Mixed secondary bases result from the primary by treatment with methyl iodide, etc. (*Hofmann*), (see p. 378).

This reaction does not usually stop short with the introduction of one alcoholic radicle, but extends further with the formation of tertiary bases. In order to avoid this, the alkyl iodide etc. may be allowed to act upon the acetylated primary bases, *e.g.* acetanilide [or upon their sodium compounds (*Hepp*),] and the resulting acetyl compound be saponified :

$$C_6H_5.NH(C_2H_3O) + CH_3I = C_6H_5.N(CH_3)(C_2H_3O) + HI.$$

The secondary bases are separated from the tertiary by treatment with nitrous acid (see below, under Nitrosamines).

2. The purely aromatic secondary amines result upon heating the primary bases with their hydrochloric acid salts :

$$C_6H_5.NHH + C_6H_5.NH_2HCl = \begin{matrix}C_6H_5\\C_6H_5\end{matrix}>NH, HCl + NH_3.$$

"Unsymmetrical" bases (*i.e.* those containing two different radicles) have also been prepared in this way.

3. Diphenylamine can further be got by heating phenol with aniline zinc chloride, (B. **17**, 2639), and :

4. By the action of bromo-benzene upon potassium-aniline.

Behaviour. 1. The mixed secondary bases have strongly marked basic properties, while the purely aromatic have not, (cf. p. 374).

2. For the breaking up of the mixed bases by hydrochloric acid, see p. 377.

3. The hydrogen of the imido-group is replaceable by an alcoholic or acid radicle, and also by potassium or sodium :

$$(C_6H_5)_2NH + CH_3I = HI + \underbrace{(C_6H_5)_2N(CH_3)}_{\text{Methyl-diphenylamine.}}$$

$$(C_6H_5)_2NH + (C_2H_3O)_2O = C_2H_4O_2 + \underbrace{(C_6H_5)_2N(C_2H_3O)}_{\text{Acetyl-diphenylamine.}}$$

4. The secondary bases give neither the iso-nitrile nor the "mustard oil" reaction (p. 124).

5. With nitrous acid, nitrosamines are formed, (cf. p. 125):

$$C_6H_5NH(CH_3) + NO.OH = H_2O + \underbrace{C_6H_5.N(NO).(CH_3)}_{\text{Phenyl-methyl-nitrosamine.}}$$

These **Nitrosamines** are neutral oily liquids insoluble in water, which regenerate the secondary bases when heated with stannous chloride or with alcohol and hydrochloric acid, and which yield hydrazines with mild reducing agents.

They serve for preparing the secondary bases pure, since they alone are precipitated by sodium nitrite as non-basic oils from the acid solution of a mixture of primary, secondary and tertiary bases. When such nitrosamines are digested with alcoholic hydrochloric acid, a molecular rearrangement takes place and compounds of the nature of nitroso-dimethyl-aniline (p. 374) are formed, the nitroso-group going into the nucleus, (*O. Fischer* and *Hepp*, B. **19**, 2991; **20**, 1247):

$$C_6H_5—N(NO)—CH_3 = C_6H_4(NO)—NH.CH_3.$$

C. Tertiary Monamines.

These also are either purely aromatic or mixed (fatty-aromatic) bases.

Modes of formation. 1. The latter result upon alkylating the primary or secondary bases (cf. p. 378), which, however, may be heated with methyl alcohol and hydrochloric acid instead of methyl chloride or iodide.

2. Tri-phenylamine, a purely aromatic base, is formed by the action of bromo-benzene upon di-potassium-aniline:

$$C_6H_5NK_2 + 2C_6H_5Br = (C_6H_5)_3N + 2KBr.$$

Behaviour. 1. Unlike the mixed (fatty-aromatic) amines, the purely aromatic tertiary amines are incapable of forming salts.

2. They do not yield iso-nitriles with $CHCl_3$, iso-thiocyanates with CS_2, or acid derivatives with acid chlorides, but they do yield quaternary compounds with methyl iodide.

3. Nitrous acid acts upon the tertiary aromatic bases (which thereby differ from the tertiary bases of the fatty series) with the formation of nitroso-compounds which contain the NO-group linked to the benzene nucleus:

$$C_6H_5.N.(CH_3)_2 + NO.OH = \underbrace{C_6H_4(NO).N(CH_3)_2}_{\text{Nitroso-dimethyl-aniline.}} + H_2O.$$

Such nitroso-derivatives are, in contradistinction to the nitrosamines already mentioned, changed into amido-compounds (diamines) by reduction (see below). For the constitution of these nitroso-bases, see also p. 388.

D. The Quaternary Bases

correspond entirely with the quaternary bases of the fatty series. Trimethyl-phenyl-ammonium hydroxide, $C_6H_5.N(CH_3)_3.OH$, for instance, is a colourless, strongly alkaline, bitter substance which breaks up into dimethyl-aniline and methyl alcohol when heated. Some of the tertiary amines however are not capable of yielding ammonium compounds.

E. Diamines, Triamines, etc.

Formation. 1. By reduction of the di- (and poly-) nitro-hydrocarbons or of the nitro-amido-compounds. In this way the phenylene diamines, $C_6H_4(NH_2)_2$, result from the dinitro-benzenes (see table, p. 375). The *o*- and *p*-diamines are best obtained from the *o*- and *p*-nitro amido-compounds (p. 387).

Tetramido-benzene results in an analogous manner by reducing the doubly nitrated *m*-diamido-benzene.

2. Further, a new amido-group can be introduced in the *p*-position into a monamine, especially a secondary or tertiary such as $C_6H_5-N(CH_3)_2$, by first transforming the latter into an azo-dye (*e.g.* benzene-azo-dimethyl-aniline), by uniting it with diazo-benzene chloride, and decomposing this by reduction. (See the Azo-compounds.)

Tri-amido compounds can be prepared in a manner exactly analogous.

3. For the preparation of diamines from nitroso-compounds of tertiary amines, see Amido-dimethyl-aniline, $C_6H_4(NH_2)[N(CH_3)_2]$.

Behaviour. The diamines and polyamines are solid compounds which crystallize in tables or plates and distil unchanged. They are soluble in water, especially upon warming. Though originally without colour, most of them quickly become brown in the air, their instability increasing with the number of amido-groups present. In accordance with the readiness with which they are oxidized, they frequently yield characteristic colourations with ferric chloride, *e.g.* *o*-phenylene-diamine a dark red, and 1 : 2 : 3-tri-amido-benzene a violet and then a brown colour.

The three isomeric varieties of diamines differ materially in their behaviour:

(*a*) **Ortho-diamines.** 1. Ferric chloride yields a yellowish-red crystalline precipitate of diamido-phenazine hydrochloride with a solution of *o*-phenylene-diamine.

2. The mono-acyl compounds of the *o*-diamines change into derivatives of imido-azole (A. **273**, 269), the so-called "*Benzimido-azoles*" or "*Anhydro-bases*," through the formation of intramolecular anhydride; thus, by the reduction of *o*-nitracetanilide by tin and hydrochloric acid, there results methyl-benzimido-azole, which may also be regarded as a derivative of ethenyl-amidine, $CH_3-C{\lt}^{NH}_{NH_2}$ (*i.e.* as phenylene-ethenyl-amidine, A. **209**, 339):

$$C_6H_4<^{NH-CO.CH_3}_{NO_2} + 3H_2 - 2H_2O = C_6H_4<^{NH-CO.CH_3}_{NH_2}$$
$$= C_6H_4<^{NH}_{N}>C-CH_3 + H_2O.$$

Compounds of this nature are also obtained by heating *o*-diamines with acids.

3. A similar reaction takes place between aldehydes and diamine hydrochlorides, with the formation of dihydro-imido-azole derivatives, the so-called "aldehydine bases," HCl being set free (*Ladenburg*, B. **11**, 590; **19**, 2025).

4. Glyoxal and many of the α-diketones yield quinoxaline and its derivatives with *o*-diamines, and the α-ketone-alcohols react in an analogous manner, benzoïn (*e.g.*) yielding dihydro-quinoxaline. With CSNH, isothiocyanates are formed (A. **221**, 1).

5. Nitrous acid converts the *o*-diamines into the so-called "azimido-compounds," compounds which contain three atoms of nitrogen, *e.g.* *o*-phenylene-diamine into azimido-benzene, = amido-azo-phenylene, $C_6H_4<^{NH}_{N}>N$ (B. **9**, 219, 1524; **15**, 1878, 2195; **19**, 1757).

(*b*) **Meta-diamido-bases.** 1. These form yellow-brown dyes with nitrous acid, even when only traces of the latter are present (see Azo-colouring matters).

2. They yield azo-dyes with diazo-benzene chloride (see Chrysoïdin).

3. With nitroso-dimethyl-aniline, or on oxidation together with para-diamines, blue colouring matters are obtained, and, upon boiling, red (see Toluylene red).

4. With CNSH, phenylene-di-ureas are formed (A. **221**, 1).

(*c*) **Para-diamido-compounds.** 1. When warmed with Fe_2Cl_6 or, better, with $MnO_2 + H_2SO_4$, quinone, $C_6H_4O_2$ (or a homologue) results and may be recognized by its odour.

2. All *p*-diamines which contain a primary NH_2-group yield violet or blue colouring matters containing sulphur and belonging to the thio-diphenylamine group (p. 389), when Fe_2Cl_6 is added to their dilute acid solution containing sulphuretted hydrogen.

3. By oxidizing para-diamines, containing one amido-group, together with a monamine or a meta-diamine, indamines are produced.

Aniline.

Aniline, amido-benzene, *phenylamine*, $C_6H_5.NH_2$.

Was first obtained in 1826 by *Unverdorben*, from the dry distillation of indigo, and termed by him "crystalline"; then *Runge* found it in coal tar in 1834 and called it "cyanol." In 1841 *Fritsche* prepared it by distilling indigo with potash and gave it the name of aniline, while in 1842 *Zinin* obtained it by the reduction of nitro-benzene and called it "benzidam." It was accurately investigated by *A. W. Hofmann* in 1843.

Occurrence. In coal tar and also in bone oil.

Preparation. Since 1864 aniline has been prepared on a manufacturing scale by reducing nitro-benzene with iron filings and a regulated quantity of hydrochloric acid, and distilling with steam. It is a colourless, oily, strongly refracting liquid of weak but peculiar odour, which quickly turns yellow or brown in the air and is finally converted into a resin. M. Pt. - 8°, B. Pt. 183°, Sp. Gr. at 0° 1·036. It dissolves in 31 parts of water, has no action upon litmus, and is a weaker base than ammonia in the cold, but displaces the latter at higher temperatures. It is poisonous, burns with a smoky flame, and is a good solvent for many compounds which are otherwise difficult of solution, *e.g.* indigo and sulphur. The salts have an acid reaction.

The *behaviour* of aniline has been investigated with the utmost care. Oxidation in alkaline solution leads to azo-benzene, while arsenic acid produces chiefly violaniline, $C_{18}H_{15}N_3$, a violet colouring matter which also results under the oxidizing influence of nitro-benzene. A solution of free aniline is temporarily coloured violet by one of bleaching powder, this reaction being an extremely delicate one. A solution in concentrated H_2SO_4 is first coloured red and then blue by a small grain of bichromate of potash. A solution of $K_2Cr_2O_7$ produces in an acid solution of aniline sulphate a dark green and then a black precipitate of aniline black, which finally goes into quinone, $C_6H_4O_2$. A mixture of aniline and toluidine is oxidizable to magenta, mauveïne, etc., and a mixture of aniline and *p*-diamines to safranines (p. 541).

Chlorine yields trichlor-aniline and iodine mon-iodo-aniline, while chlorate of potash and hydrochloric acid produce chloranil. For the action of N_2O_3, see diazo-compounds; of HNO_3, nitraniline; and of H_2SO_4, sulphanilic acid. When aniline is heated with glycerine and concentrated sulphuric acid in the presence of nitro-benzene, quinoline is obtained; when it is boiled with sulphur, thio-aniline, $(C_6H_4.NH_2)_2S$; and when it is heated with urea, diphenyl-urea, $CO(NHC_6H_5)_2$, with elimination of NH_3. Many reactions analogous to the last-named are known.

By the action of formic aldehyde upon aniline under certain conditions, there is produced "Anhydro-formaldehyde-aniline" $(C_6H_5—N{=}CH_2)_x$

(colourless crystals); and this is condensed by hydrochloric acid in presence of more aniline to diamido-diphenyl-methane (which see).

Salts. Aniline hydrochloride, $C_6H_5.NH_2$, HCl: large colourless tables which become greenish-grey in the air and distil unchanged. Aniline sulphate, $(C_6H_7N)_2H_2SO_4$: beautiful white plates, difficultly soluble in water. The double salt with platinic chloride, $(C_6H_7N, HCl)_2$, $PtCl_4$, crystallizes in moderately soluble yellow plates.

Substitution Products of Aniline.

Aniline is much more readily substituted by halogens than benzene, an aqueous solution of chlorine or bromine causing substitution of as many as three atoms of hydrogen, while iodine produces mono-iodaniline. In the preparation of **mono-chlor-** (or **brom-**) **aniline**, the aniline must be "protected" by using it in the form of its acetyl compound, acetanilide. When this is suspended in water, it is mostly transformed by chlorine into *p*-**chlor-acetanilide**, which readily yields *p*-chlor-aniline on saponification; the latter forms colourless crystals, M. Pt. 71°, B. Pt. 231°. The *o*- and *m*-compounds, which are both liquid, are prepared indirectly, *e.g.* by the reduction of *o*- or *m*-chloro- (or bromo-) nitro-benzene.

The basic character is weakened in the mono-chlor- (and brom-) anilines by the entrance of the halogen, this being the case particularly in the *o*-compounds. It is still more striking in *a*-**trichlor-aniline**, $C_6H_2Cl_3(NH_2)$ (crystals, volatile without decomposition), which no longer combines with acids. *o*- and *p*-chlor-anilines are only capable of taking up two more atoms of chlorine with the formation of trichlor-aniline: $NH_2:Cl:Cl:Cl = 1.2.4.6$; *m*-chlor-aniline, on the other hand, can be further chlorinated to **tetra-** and **penta-chlor-aniline**.

The **Brom-anilines** resemble these in every respect.

Nitranilines.

Aniline is likewise attacked far more violently than benzene by concentrated nitric acid, and therefore, when it is wished to prepare the mono-nitro-compounds, the aniline must again be "protected," either by using its acetyl compound or by nitrating in presence of excess of concentrated sulphuric acid. In the latter case all three nitranilines result, the *m*-compound preponderating. When acetanilide is nitrated, *p*-**Nitracetanilide**, $C_6H_4(NO_2)(NH.C_2H_3O)$, together with some of the *o*-compound, result, both of them being easily saponified by potash or hydrochloric acid.

The *o*- and *p*-nitranilines are also formed upon heating *o*- and *p*-chloro- or bromo-nitro-benzenes, or the ethers of the corresponding *o*- and *p*-nitro-phenols, $C_6H_4(NO_2)(O.C_2H_5)$, or these nitro-phenols themselves with ammonia to 180°, (cf. B. **19**, 1749). *o*-Nitraniline may also be prepared by nitrating acetyl-sulphanilic acid, (B. **19**, 985).

The nitranilines are further obtained by the partial reduction of the corresponding dinitro-benzenes, *e.g.* by means of sulphide of ammonium.

The three nitranilines crystallize in yellow needles or prisms, readily soluble in alcohol but only very slightly in water, (cf. table, p. 375). The *o*- and *m*-compounds are volatile with steam, but not *p*-nitraniline. They go into phenylene-diamines on reduction.

The *o*- and *p*-nitranilines are converted into nitro-phenols when boiled with alkalies, the former more easily than the latter, thus:

$$C_6H_4(NO_2)(NH_2) + H.OH = C_6H_4(NO_2)OH + NH_3.$$

Di- and **tri-nitranilines**, $C_6H_3(NO_2)_2(NH_2)$ and $C_6H_2(NO_2)_3(NH_2)$, are likewise known; the latter, which is termed **Picramide**, and which crystallizes in yellow needles, M. Pt. 188°, comports itself as the amide of picric acid, since it is readily transformed into the latter compound by saponifying agents, (cf. p. 350).

For **Aniline-sulphonic acids**, see p. 410.

Alkylated Anilines.

Methyl-aniline, $C_6H_5NH(CH_3)$ (*Hofmann*), is obtained from the methyl-aniline of commerce (from aniline hydrochloride and methyl alcohol) either by means of its nitroso-compound or as given at p. 380 (cf. B. 10, 327, 588). It is lighter than water, and has an odour like that of aniline but stronger and more aromatic.

Its sulphate is soluble in ether and non-crystallizable. A solution of bleaching powder colours it violet and then brown. For its transformation into *p*-toluidine, see p. 377.

Methyl-aniline-nitrosamine, $C_6H_5.N(NO)(CH_3)$, is a yellow oil of aromatic odour without basic properties, which can be distilled with steam but not alone. It shows the *Liebermann* (nitroso) reaction, giving an intense "king's-blue" colouration when it is warmed with phenol and sulphuric acid, and the mixture then diluted with water and saturated with

caustic potash. This reaction is characteristic of all the nitrosamines and of many other nitroso-compounds (see B. **15**, 1529).

Di-methyl-aniline, $C_6H_5.N(CH_3)_2$ (*Hofmann*), is an oil of sharp basic odour, solidifying in the cold. Its salts are not crystallizable. It combines with methyl iodide, even in the cold, to the compound $N(C_6H_5)(CH_3)_3I$, which breaks up into its components upon distillation. The corresponding ammonium base is mentioned on p. 382. Bleaching powder only colours dimethyl aniline a pale yellow. The H-atom in it, which is in the *p*-position as regards the $N(CH_3)_2$, is easily exchangeable, *e.g.* for a nitroso-group, when acted on by N_2O_3. Dimethyl-aniline consequently yields compounds of somewhat complex composition with acid chlorides, aldehyde, etc.; for example, tetramethyl-diamido-benzophenone or, finally, methyl violet with carbonyl chloride, $COCl_2$, leuco-malachite green with benzoic aldehyde, etc. Mild oxidizing agents, such as chloranil, convert it into methyl violet.

p-**Nitroso-dimethyl-aniline**, $C_6H_4(NO).N(CH_3)_2$, crystallizes in beautiful green plates or tables of M. Pt. 85°; its HCl-salt forms yellow needles. It is used for the preparation of dyes (methylene blue, indophenol, gallocyanine, etc.). It is oxidized by $KMnO_4$ or K_3FeCy_6 to *p*-**Nitro-dimethyl-aniline**, $C_6H_4(NO_2).N(CH_3)_2$, M. Pt. 162° (a compound which is also obtained directly together with the *m*-compound by the nitration of dimethyl-aniline), and is reduced by nascent hydrogen to amido-dimethyl-aniline, $C_6H_4(NH_2).N(CH_3)_2$, which belongs to the *p*-diamines (p. 393). Boiling with soda converts it into nitroso-phenol and dimethylamine.

p-**Nitroso-aniline**, $C_6H_4(NO)NH_2$. For constitution, see above. This is prepared by the action of ammonium acetate upon nitroso-phenol, and crystallizes in blue needles (B. **20**, 2471). *p*-**Nitroso-monomethyl-aniline**, $C_6H_4(NO)(NH.CH_3)$, results by a molecular transformation from the action of hydrochloric acid in alcoholic solution upon methyl-aniline nitrosamine; it forms green plates or steel-blue prisms (cf. p. 381).

Nitroso-phenol is a derivative of quinone, viz.: $C_6H_4\left\langle\begin{matrix} O \\ \cdot \\ N.OH \end{matrix}\right.$; nitroso-dimethyl-aniline therefore probably contains no nitroso- but an isonitroso-group, in accordance with the formulæ:

$$C_6H_4\left\langle\begin{matrix} N \\ \cdot \\ N(CH_3)_2 \end{matrix}\right\rangle O. \qquad\qquad C_6H_4\left\langle\begin{matrix} N.OH \\ \cdot \\ N(CH_3)_2Cl. \end{matrix}\right.$$

The free base. — The hydrochloride.

The same applies to nitroso-aniline and nitroso-methyl-aniline.

Di- and Triphenylamines.

Diphenylamine, $(C_6H_5)_2NH$ (*Hofmann*), crystallizes in white plates of flowery odour and burning taste which are almost insoluble in water, but readily soluble in alcohol, ether and ligroïn. The hydrochloride, $C_{12}H_{11}N$, HCl, is a white crystalline meal which turns blue in the air. A solution of diphenylamine in concentrated H_2SO_4 is coloured an intense blue by traces of nitric acid, this reaction being a very delicate test for the latter. When diphenylamine is heated with formic acid and zinc chloride, it yields acridine. It is used for the preparation of diphenylamine blue and aurantia.

Diphenyl-nitrosamine, $(C_6H_5)_2N.NO$, is obtained by the use of ethyl nitrite and crystallizes in bright glancing yellowish tables. *o*-**Dinitrodiphenylamine,** $(C_6H_4.NO_2)_2NH$, forms red needles, and the analogous *p*-compound yellow prisms. **Hexa-nitro-diphenylamine** crystallizes in yellow prisms and has the properties of a weak acid, this being due to the acidifying influence of the nitro-groups upon the imido-hydrogen; its ammonium salt is a yellow dye, which was formerly used under the name of *Aurantia.* For the **Amido-** and **Oxy-compounds** of diphenylamine, which are tabulated on p. 375, and the colouring matters derivable from them, see also Safranine.

Methyl-diphenylamine, $(C_6H_5)_2N.CH_3$, is a liquid which results on methylating diphenylamine; it also is employed on a manufacturing scale.

Thio-diphenylamine, $C_{12}H_9NS$, $= NH\langle{}^{C_6H_4}_{C_6H_4}\rangle S$, is obtained by heating diphenylamine with sulphur. Yellowish plates; M. Pt. 180°. May be distilled unchanged.

Triphenylamine, $N(C_6H_5)_3$, forms large tables (see p. 374).

Indamines and Indophenols.

The compounds designated **Indamines** (*Nietzki*) are those green or blue colouring matters which are produced by the action of nitroso-dimethylaniline upon amines, *e.g.* dimethyl-aniline, or by the conjoint oxidation of *p*-diamines and monamines in the cold.

The simplest representative of this class is the indamine "**Phenylene Blue,**" $C_{12}H_{11}N_3$, $= N\left<\begin{matrix}C_6H_4.NH_2\\ C_6H_4.NH\end{matrix}\right.$, which results from the oxidation of a mixture of aniline and *p*-phenylene-diamine, and is converted by reduction into *p*-diamido-diphenylamine, $NH(C_6H_4.NH_2)_2$ (p. 375).

"**Dimethyl-phenylene Green,**" *tetramethyl-indamine chloride*, $C_{16}H_{19}N_3$, is obtained in an analogous manner from *p*-amido-dimethyl-aniline and dimethyl-aniline, and yields tetramethyl-*p*-diamido-diphenylamine, $NH[C_6H_4.N(CH_3)_2]_2$ (p. 375), on reduction. The indamines are unstable compounds, but are of importance as being intermediate products in the manufacture of safranine.

Oxygenated compounds, *Witt's* "**Indophenols,**" are likewise derived here by the exchange of NH_2 or $N(CH_3)_2$ for OH, which is achieved by warming with alkali; *e.g.* **Phenol Blue** (indo-aniline), $N\left<\begin{matrix}C_6H_4.N(CH_3)_2\\ C_6H_4.O\end{matrix}\right.$, is produced by the oxidation of amido-dimethyl-aniline with phenol. Its analogue, α-**Naphthol Blue**, $N\left<\begin{matrix}C_6H_4.N(CH_3)_2\\ C_{10}H_{16}.O\end{matrix}\right.$, prepared by means of naphthol (p. 505), is a colouring matter which finds technical application. Such compounds exchange $N(CH_3)_2$ for OH when boiled with a solution of NaOH; thus, from phenol blue there results **Indophenol** ("quinone-phenol-imide"), $N\left<\begin{matrix}C_6H_4.OH\\ C_6H_4.O\end{matrix}\right.$, a dye of phenolic nature (p. 411), which dissolves in alcohol to a red, and in alkali or ammonia to a blue solution. It may also be obtained by the action of phenol upon quinone chlor-imide (see Quinones):

$$\underset{\text{Quinone chlor-imide.}}{C_6H_4\left<\begin{matrix}O\\ |\\ N.Cl\end{matrix}\right.} + C_6H_5OH = C_6H_4\left<\begin{matrix}O\\ |\\ N—C_6H_4.OH,\end{matrix}\right. = \underset{\text{Indophenol.}}{N\left<\begin{matrix}C_6H_4.OH\\ C_6H_4.O\end{matrix}\right.} + HCl;$$

and also by the oxidation of *p*-amido-phenol with phenol. Its leuco-compound is *p*-**Dioxy-diphenylamine**, $NH(C_6H_4.OH)_2$, a substance which unites in itself the properties of diphenylamine and a diatomic phenol. (See p. 423; cf. B. 16, 2843; 18, 2912.)

Acid Derivatives of Aniline, Anilides.

Phenyl-sulphamic acid, $C_6H_5.NH.(SO_3H)$, is the type of the organic sulphamic acids, $SO_2<^{OH}_{NR_2}$, compounds as yet but little known, which result from the action of sulphuric oxychloride or anhydride on the amines in the cold (*e.g.* in chloroform solution). The free acids are very unstable, like ethyl-sulphuric acid; but the salts, *e.g.* the barium salt, are more stable and crystallizable (cf. B. **23**, 1653).

Formanilide, $C_6H_5.NH.(CHO)$, from aniline and formic acid, is worthy of note, because its sodium salt reacts according to the formula $C_6H_5.NNa.(CHO)$, but its silver salt according to the formula $C_6H_5.N=CH(OAg)$. (Cf. B. **23**, 2274, Ref. 659.) The latter corresponds to those isomers of the amides, the imido-hydrates and imido ethers (p. 200).

Acetanilide, $C_6H_5.NH.(C_2H_3O)$, is most conveniently prepared by boiling aniline with glacial acetic acid for several days, or by the action of acetic anhydride upon aniline in presence of caustic soda solution (B. **23**, 2962). It crystallizes in beautiful white prisms which are readily soluble in hot water, alcohol, ether and benzene; M. Pt. 115°, B. Pt. 304°. It is easily saponifiable (cf. p. 379). Its imido-hydrogen is replaceable by sodium with the formation of the crystalline **Sodium-acetanilide**, $C_6H_5.N.Na(C_2H_3O)$, which is again decomposed by water (see p. 195). Acetanilide is used, under the name of "antifebrine," as a medicine in cases of fever.

Thio-acetanilide, $CH_3—CS.NHC_6H_5$, results upon heating acetanilide with P_2S_5 (analogously to aceto-thiamide, p. 199), and from it **Imido-thio-compounds**, **Amidines**, etc. can be prepared. Acetanilide yields the dye Flavaniline when heated with zinc chloride. **Methyl-acetanilide**, $C_6H_5.N(CH_3)(C_2H_3O)$, is used as a specific against headache.

In nearly all those compounds of the fatty series which are ammonia derivatives of alcohols, acids or alcohol-acids, and which still contain unreplaced ammoniacal hydrogen, the latter can be substituted either wholly or partially by phenyl, for the most part indirectly. The number of these phenylated

(tolylated, xylylated, etc.) compounds is thus extremely large. Among them may be mentioned:

Phenyl-glycocoll, $\begin{matrix} CH_2—NH.C_6H_5 \\ CO·OH \end{matrix}$, from chloracetic acid and aniline; **Phenyl-imido-butyric acid**, $CH_3—C(NC_6H_5)—CH_2—CO_2H$, from aniline and aceto-acetic ether; **Carbanilide** or diphenyl-urea, $CO(NHC_6H_5)_2$, from aniline and carbon oxychloride, (cf. p. 291); **Phenyl cyanate**, $CO:N.C_6H_5$, a sharp-smelling liquid exactly analogous to the cyanic ethers, and whose vapour gives rise to tears, from $COCl_2$ and fused aniline hydrochloride; **Phenyl isothiocyanate**, $C_6H_5N:CS$, (B. Pt. 222°), a liquid possessing all the characteristics of the mustard oils; **Diphenyl-thio-urea**, $CS(NHC_6H_5)_2$, from aniline and carbon bisulphide, (glancing plates, M. Pt. 154°, decomposed into phenyl isothiocyanate and aniline by boiling with concentrated HCl); **Mono-**, **Tri-**, and **Tetra-phenyl-thio-ureas**; **Phenylated guanidines**, etc. (cf. table, p. 375).

Homologues of Aniline.

1. The three **Toluidines**, $C_6H_4(CH_3)(NH_2)$, result from the reduction of the three nitro-toluenes, *p*-toluidine (*Muspratt* and *Hofmann*, 1845) being solid, and *o*-toluidine liquid; they are also present in coal tar.

The crude nitro-toluene of commerce yields a mixture of *o*- and *p*- with a little *m*-toluidine upon reduction; the two first may be separated from one another, *e.g.* by taking advantage of the relatively sparing solubility of *p*-toluidine oxalate, (cf. B. **16**, 908).

***m*-Toluidine**, which is liquid, may be prepared from *m*-nitro-toluene or *m*-nitro-benzaldehyde, (cf. B. 15, 2009).

The boiling points of the three isomeric toluidines are almost identical (see table, p. 375), but the melting points of their acetyl compounds differ widely, the *o*-compound melting at 107°, the *p*- at 147°, and the *m*- at 65°; these are therefore of value for the characterization of the toluidines. *o*-Toluidine is coloured violet by a solution of chloride of lime, and blue by sulphuric and nitrous acids and also by ferric chloride, but not *p*-toluidine. For their conversion into fuchsine by oxidation, see p. 490. If, during oxidation, the amido-group be protected by the introduction of acetyl, the methyl can be oxidized to carboxyl and in this way an (acetyl derivative of) amido-benzoic acid obtained, while the amido-compounds are transformed into azo-compounds by $KMnO_4$.

Compounds such as **Methyl-** and **dimethyl-*p*-toluidines**, **acet-toluide**, $C_6H_4(CH_3).NH(C_2H_3O)$, **di-tolylamine**, $(C_6H_4.CH_3)_2NH$, **tolyl-phenyl-amine**, $NH[C_6H_5](C_6H_4.CH_3)$, **nitro-toluidines**, $C_6H_3(CH_3)(NO_2)(NH_2)$, etc., have been prepared in large numbers, and are in every respect similar to the corresponding phenyl compounds.

2. Isomeric with the toluidines is:

Benzylamine, $C_6H_5—CH_2.NH_2$, the alcoholic amine of benzyl alcohol, a colourless basic liquid which distils unchanged. It is best prepared, at first as the acetyl compound, $C_6H_5—CH_2.NH(C_2H_3O)$, by heating benzyl chloride, $C_6H_5—CH_2Cl$, with acetamide, $NH_2(C_2H_3O)$. Its behaviour is entirely analogous to that of methylamine, as the phenyl derivative of which it is to be regarded, (cf. p. 380).

3. **Xylidines**, $C_6H_3(CH_3)_2.NH_2$. According to theory, these may exist in six modifications, all of which are known. **Amido-*o*-xylene** ($CH_3:CH_3:NH_2$ = 1:2:4) is solid, melting at 49°, while the other five are liquid. The boiling points lie between 212° and 226°. The xylidine of commerce contains five of these compounds, but principally ***m*-xylidine** ($CH_3:CH_3:NH_2$ = 1:3:4), B. Pt. 212°, and ***p*-xylidine** (1:4:2); it is used for the manufacture of azo-dyes.

4. **Amido-trimethyl-benzenes**, $C_6H_2(CH_3)_3NH_2$. The hydrochloride of amido-trimethyl-benzene is formed when HCl-xylidine is heated with methyl alcohol to about 300°. In this way there have been prepared **ψ-(Pseudo-)cumidine** or *amido-pseudo-cumene* ($CH_3:CH_3:CH_3:NH_2$ = 1:2:4:5), M. Pt. 63°, B. Pt. 235°, and **Mesidine** or *amido-mesitylene* (1:3:5:2), a liquid, B. Pt. 230°. ψ-Cumidine is also used for manufacturing azo-dyes.

Isomeric with the above bases are **amido-ethyl-benzene** $C_6H_4.(NH_2)(C_2H_5)$, and **amido-propyl-benzene**, $C_6H_4(NH_2)(C_3H_7)$, of which the *p*-modifications, for instance, are obtained by heating aniline with the alcohol in question and chloride of zinc.

5. **Amido-isobutyl-benzene**, $C_6H_4(NH_2)(C_4H_9)$, has likewise been prepared.

Tetramethyl-amido-benzenes (*amido-durene*, *prehnidine*), $C_6H(NH_2)(CH_3)_4$, ***m*-isocymidine**, $C_6H_3(NH_2)(CH_3)(C_3H_7)$, and **penta-methyl-amido-benzene**, $C_6(NH_2)(CH_3)_5$, are also known.

Diamines, Triamines, etc.

1. Of the **Phenylene-diamines**, $C_6H_4(NH_2)_2$, the meta-compound (*Zinin*, 1844) is the most easily prepared, by reducing *m*-dinitro-benzene. It

crystallizes in tables. Nitrous acid converts it into Bismarck brown, the presence of the merest trace of this acid being shown by the yellow colouration it gives with the diamine (cf. B. **14**, 1015). **Para-phenylene-diamine** (*Hofmann*, 1863) crystallizes in plates, and its HCl-salt in white tables; an acid solution of it yields the violet dye thionine (p. 543) with H_2S and Fe_2Cl_6. A mixture of the *p*- and *m*-compounds ultimately yields a diamido-phenazine upon oxidation. Its unsymmetrical dimethyl-derivative, ***p*-amido-dimethyl-aniline**, $C_6H_4(NH_2)[N(CH_3)_2]$, which may be prepared as given at p. 388, but most easily by the reduction of the azo-dye helianthin (p. 405; B. **16**, 2235), gives methylene blue with Fe_2Cl_6 and H_2S, this being the most delicate test for sulphuretted hydrogen known, and it is coloured a magnificent purple by Fe_2Cl_6 in dilute neutral solution. **Ortho-phenylene-diamine** (*Griess*, 1861) is transformed into hydro-phenazine (p. 539) when heated with pyrocatechin, and into a diamido-phenazine upon oxidation with ferric chloride (cf. B. **23**, 841). A *p*-**Diamido-hexamethylene** is known (B. **22**, 2168).

2. *o*-*p*-**Toluylene-diamine**, $C_6H_3(CH_3)(NH_2)_2$ (1:2:4), is, as a *m*-diamine, easily obtained by reduction of the common dinitro-toluene (p. 372). It is used for the preparation of toluylene red, etc. *m*-*p*-**Toluylene-diamine**, $C_6H_3(CH_3)(NH_2)_2$ (1:3:4), is the *o*-diamine which is most easily prepared, viz., by nitrating aceto-*p*-toluide, saponifying and reducing.

3. The **Xylylene-diamines**, $C_6H_2(CH_3)_2(NH_2)_2$, are homologous with the above.

4. The **Tetramido-benzenes**, $C_6H_2(NH_2)_4$ (p. 383; B. **20**, 328; **22**, 1648; **23**, 2815; **25**, 283), and **Pentamido-benzene**, $C_6H(NH_2)_5$ (B. **21**, 1541, 1706), *are very unstable and easily oxidized.*

XXI. DIAZO- AND AZO-COMPOUNDS; HYDRAZINES.

A. Diazo-Compounds.

The primary amido-compounds of the benzene series differ characteristically from those of the fatty series in their behaviour towards nitrous acid. The latter are converted into alcohols by N_2O_3 without the formation of intermediate products, (cf. p. 124):

$$C_2H_5.NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O.$$

The aromatic amines can indeed undergo an analogous transformation, but there result in their case well-characterized intermediate products, the so-called diazo-compounds, which are of especial interest both scientifically and technically (cf. p. 395). They were discovered by *P. Griess* in 1860

and were carefully investigated by him, (A. **121**, 257; **137**, 39); their constitution was elucidated by *Kekulé*.

Formation. When nitrogen trioxide is led into a cream of aniline nitrate and dilute nitric acid, the aniline salt dissolves and a liquid is obtained from which alcohol and ether precipitate beautiful long white needles of diazo-benzene nitrate, $(C_6H_5N_2).NO_3$. These are tolerably stable in dry air but quickly decompose in moist, and they are distinguished by the violence with which they explode when heated or struck. The base itself, diazo-benzene (p. 398), appears to have the formula $(C_6H_5—N_2)OH$, just as the base KOH corresponds to the salt KNO_3.

In a similar manner other salts of diazo benzene, *e.g.* the chloride, $C_6H_5N_2.Cl$, and the sulphate, $(C_6H_5N_2).SO_4H$, are obtained from aniline hydrochloride and sulphate in the presence of free acid. Double salts with $PtCl_4$, $AuCl_3$, etc., are also known. The homologues of aniline and many diamines show a similar behaviour, *e.g.* *p*-toluidine yields salts of diazo-toluene, *e.g.* $C_6H_4(CH_3)N_2.Cl$.

Most of the diazo-compounds are prepared only in aqueous solution, and not in the solid form, on account of their instability and tendency to explode. One mol. aniline, for instance, is dissolved in two or more mols. hydrochloric acid, and the calculated quantity of a solution of sodium nitrite is allowed to flow into it, the whole being cooled by ice. The liquid must remain clear and no nitrogen to speak of must be evolved. Any excess of nitrous acid can be got rid of by blowing air through the solution. Occasionally the amido-compound dissolved in concentrated sulphuric acid is treated with N_2O_3; or an alcoholic solution of amyl or ethyl nitrite and a mineral acid are used.

The formation of the diazo-compounds is shown by the following equation:

$$\begin{matrix} C_6H_5.N \vdots H_2, H \vdots NO_3 \\ N \vdots O_2H \quad \vdots \end{matrix} = \underbrace{C_6H_5.N{=}N.NO_3}_{\text{Diazo-benzene nitrate.}} + 2H_2O.$$

The conversion of amido- into diazo-compounds is termed "diazótizing."

The constitution of the diazo-compounds, *e.g.* $C_6H_5–N{=}N–Cl$ or $C_6H_5N{=}N—SO_4H$, follows especially from these two re-

actions: 1, from their transformation into hydrazines upon reduction; 2, from the formation of azo-dyes by the action of diazo-compounds upon many amines and phenols.

Diazo-benzene, $C_6H_5—N=N.OH$, also appears frequently to enter into reaction in its "pseudo-form," $C_6H_5—NH—NO$ (*Caro*, *Ost*; cf. also B. **26**, 495).

Behaviour. 1. Towards water. An aqueous solution of a diazo-salt, especially one containing sulphuric acid, gives off all its nitrogen in the form of gas upon warming, and there results a phenol, thus:

$$\begin{matrix} C_6H_5.N=N.Cl \\ + OH \quad\quad H \end{matrix} = C_6H_5.OH + N_2 + HCl.$$

This reaction, which is of very universal application, therefore allows of the exchange of amidogen for hydroxyl.

The above reaction, as well as the following ones (up to 4), may be included under the term "diazotizing" for the sake of brevity.

2. Towards alcohol. When diazo-compounds, either in the solid state or dissolved in concentrated sulphuric acid, are heated to boiling with absolute alcohol, the diazo-group is generally replaced by hydrogen. In this reaction the alcohol gives up two atoms of hydrogen and goes into aldehyde:

$$\begin{matrix} C_6H_5.N=N.Cl \\ + H \quad\quad H \end{matrix} = C_6H_6 + N_2 + HCl.$$

By this means we are enabled completely to eliminate a diazo-group, and therefore an amido- one from a benzene derivative.

Instead of this reaction there occurs in many cases an exchange of the diazo-group for the alcohol radicle, $O.C_2H_5$, with the formation of ethyl ethers of phenol; thus chlorinated cresol ethyl ether results, in place of chloro-toluene, from chlorinated toluidines (B. **17**, 2703; **22**, Ref. 658).

2*a*. Under certain conditions stannous chloride in alkaline solution acts in an analogous manner (B. **22**, Ref. 741), while under others it gives rise to hydrazines (p. 406). In like manner NH_2 may be replaced by H, by first converting an amido-compound into a hydrazine, and then decomposing the latter with $CuSO_4$ (*Baeyer*, B. **18**, 89).

3. When a diazo-compound is warmed with a concentrated solution of cuprous chloride in hydrochloric acid, the diazo-group is replaced by chlorine (*Sandmeyer*, B. **17**, 1633; **23**, 1218, 1628; A. **272**, 143); the same reaction takes place on distilling the platinum double salt of the diazo-compound with soda, and sometimes on simply treating the diazo-compound itself with fuming hydrochloric acid, or with hydrochloric acid in presence of copper dust:

$$C_6H_5.N=N.Cl = C_6H_5Cl + N_2.$$

4. Warming with cuprous bromide yields in the same way a bromine compound (*Sandmeyer*, B. **18**, 1482), and treatment with hydriodic acid or potassium iodide an iodine one, while cuprous cyanide effects an exchange of the amido group for cyanogen (B. **17**, 2650):

$$2C_6H_5.N_2.Cl + Cu_2Br_2 = 2C_6H_5Br + Cu_2Cl_2 + N_2;$$
$$C_6H_5.N_2.Cl + KI = C_6H_5I + KCl + N_2; \text{ etc.}$$

The NH_2-group may further be exchanged for Br by boiling the diazo-perbromides (see Diazo-benzene perbromide) with absolute alcohol.

5. Phenyl sulphide results from diazo-benzene chloride and sulphuretted hydrogen (cf. B. **15**, 1683); nitro-benzene is formed by the action of nitrous acid in presence of cuprous oxide; benzene-sulphonic acid from sulphurous acid; benzene thiocyanate from thiocyanic acid; and phenyl cyanate from cyanic acid, etc. (cf. B. **23**, 738, 1218, 1454, 1628; **25**, 1086).

The reactions 1 to 4, which are classed together under the name of the *Griess* reaction, are invaluable for effecting the exchange of nitro- or amido-groups for OH, H, Cl, Br, I and CN, and are constantly made use of in the laboratory.

When reactions 3, 4 and 5 take place under the influence of cuprous oxide and its salts, or of copper dust, they are also included under the special name of "the *Sandmeyer* reaction."

6. Upon oxidation in alkaline solution, diazo-benzene yields—together with other products—nitroso-benzene (p. 373), and much **Phenyl-nitramine,** $C_6H_5.NH.NO_2$ (M. Pt. 46°; explodes at 98°) (see B. **26**, 471).

7. Diazo-benzene in alkaline solution unites with compounds containing the group $—CH_2—CO—$, water being eliminated. It reacts here according to the tautomeric formula $C_6H_5.NH.NO$, since *hydrazones* result, *e.g.* from acetone the diphenyl-hydrazone of mesoxalic aldehyde, $C_6H_5NH.N{=}CH—CO—CH{=}N.NHC_6H_5$ (B. **25**, 2793).

From diazo-benzene and malonic acid there is produced **Formazyl hydride,** $C_6H_5N{=}N—CH{=}N—NHC_6H_5$, together with azo-compounds and hydrazone (B. **25**, 3175, 3201).

8. When a diazo-compound acts upon a primary or secondary amine, or when N_2O_3 acts upon such an amine in the absence of acid, diazo-amido-compounds result, and these readily change into amido-azo-compounds. The latter are formed directly by the action of the diazo-compounds upon tertiary amines:

$$C_6H_5.N{=}N.Cl + NH_2.C_6H_5 = HCl + \underbrace{C_6H_5.N{=}N—NH.C_6H_5}_{\text{Diazo-amido-benzene.}};$$

$$C_6H_5.N{=}N.Cl + C_6H_5.N(CH_3)_2 = HCl + \underbrace{C_6H_5—N{=}N—C_6H_4.N(CH_3)_2}_{\text{Dimethyl-amido-azobenzene.}}.$$

Analogous reactions also take place with the *m*-diamines and with phenols, oxy-azo-compounds being formed in the latter case (see p. 402). The production of an orange-red dye by the action of diazo-compounds upon *m*-phenylene-diamine or β-naphthol is a very delicate test for the presence of the former. Diazo-amido-compounds only show this reaction in acetic acid solution.

It has been proposed to use diazo-compounds, sensitive to light, in photography (B. 23, 3131).

The salts of the diazo-compounds are colourless, and frequently crystallize well; they often decompose with violent explosion in the air or upon being kept. Most of them are easily soluble in water, slightly soluble in alcohol, and insoluble in ether.

Diazo-benzene chloride, $C_6H_5-N=N-Cl$, crystallizes in colourless needles.

Diazo-benzene nitrate, $C_6H_5-N=N.(NO_3)$ (p. 395). Long needles.

Diazo-benzene sulphate, $C_6H_5.N=N.(SO_4H)$, is a syrupy mass which solidifies to prisms; it explodes at 160°.

Diazo-benzene perbromide, $C_6H_5N=N.Br.Br_2$, is a dark brown oil, solidifying to yellow crystalline plates, which results upon the addition of HBr or KBr and bromine water to diazo-salts. Two of its atoms of bromine are only loosely linked. Ammonia converts it into diazo-benzene-imide, which is to be regarded as the phenyl derivative of hydrazoic acid, N_3H, thus:

$$C_6H_5.N=N.Br + Br_2 = C_6H_5.NBr-NBr_2 \text{ [Diazo-benzene-perbromide].}$$

$$C_6H_5.NBr-NBr_2 + NH_3 = 3HBr + C_6H_5.N\Big<\begin{matrix}N\\ \vdots\\ N\end{matrix} \text{ [Diazo-benzene-imide].}$$

In accordance with this, dinitro-diazo-benzene-imide (from dinitro-aniline) is broken up by alcoholic potash into dinitro-phenol and *hydrazoic acid*,—a method of obtaining this latter substance by means of organic compounds (see pp. 228 and 299).

When concentrated potash solution acts upon diazo-benzene nitrate, **Potassium diazo-benzene**, $C_6H_5N=N(OK)$ (cf. B. 23, 3033), is formed. It crystallizes in white glancing mother-of-pearl plates, readily soluble in water and alcohol and easily decomposable, and from its aqueous solution metallic salts precipitate other metallic compounds, *e.g.* the very explosive **Silver diazo-benzene**, $C_6H_5N=N-O.Ag$. The free **Diazo-benzene**, $C_6H_5.N=N.OH$ (?), is precipitated from the potassium salt by acetic acid as a heavy oil which rapidly decomposes of itself.

"**Azimido-benzene**," $C_6H_4\Big<\begin{matrix}N\\ NH\end{matrix}\Big>N$, results from *o*-phenylene-diamine and nitrous acid. Colourless needles, M. Pt. 98°. It possesses a weakly basic character, and is to be regarded as the intramolecular anhydride of the partially diazotized ortho-diamine. The isomeric formula, $C_6H_4\Big<\begin{matrix}N\\ |\\ N\end{matrix}\Big>NH$, represents the hypothetical "*Pseudo-azimido-benzene*," of which derivatives are known (cf. *Zincke*, A. 255, 339).

B. Diazo-amido-compounds.

The diazo-amido-compounds are pale yellow crystalline substances which are stable in the air, and do not combine with acids.

Formation. See preceding page.

Behaviour. 1. The diazo-amido-compounds behave in pretty much the same way as the diazo-compounds, since they are usually broken up in the first instance into their components,

diazo-benzene (salt) and amine, the former then entering into reaction. Thus diazo-amido-benzene, for example, yields phenol and aniline when boiled with water or hydrochloric acid, while with hydrobromic acid it gives bromo-benzene and aniline.

These reactions are easy to recognise from the accompanying evolution of nitrogen.

2. By the renewed action of nitrous acid in acid solution, they are completely transformed into diazo-compounds, *e.g.*:

$$C_6H_5.N_2.NH.C_6H_5 + NO_2H + 2HCl = 2C_6H_5.N_2.Cl + 2H_2O.$$

3. Most of them readily undergo molecular transformation into the isomeric amido-azo-compounds, (*Kekulé*).

This molecular rearrangement takes place particularly easily in presence of an amine hydrochloride, which is explained by the action of the latter upon the diazo-amido-compound, thus:

$$C_6H_5.N_2.NH.C_6H_5 + C_6H_5.NH_2 = C_6H_5.N_2.C_6H_4.NH_2 + C_6H_5.NH_2.$$

In the above reaction the aniline (*i.e.* the amine) is continually being regenerated, so that a small quantity of it suffices for the transformation (for another explanation, see B. **25**, 1376). The nitrogen of the amine here takes up the para-position with regard to the azo-group (—N=N—).

This molecular rearrangement is easy to effect in the case of the diazo-amido-compounds of aniline and also in those of *o*- and *m*-toluidine, but more difficult in the case of the *p*-compound; in *p*-toluidine the para-position is already taken up by CH_3, so that another position (the ortho-) must be occupied here. (Cf. p. 403.)

4. The imido-hydrogen of the diazo-amido-compounds is replaceable by Ag, etc.

Constitution. By the action of diazo-benzene chloride upon *p*-toluidine there results "diazo-benzene-*p*-toluide," which would thus appear to possess the formula:

$$C_6H_5—N=N—NH—C_7H_7 \qquad (I.).$$

But the same compound is also obtained from a mixture of diazo-*p*-toluene chloride and aniline, a reaction which would indicate its constitution to be:

$$C_6H_5—NH—N=N—C_7H_7 \qquad (II.).$$

It is all the more difficult to decide which of these two formulæ is the right one, from the fact that most of those "mixed diazo-amido-compounds" react as if they had both of the above constitutions. Thus, when the compound just mentioned is boiled with dilute sulphuric acid,

it yields not only phenol and *p*-toluidine (according to I.), but also aniline and *p*-cresol (according to II.). Cf. *e.g.* B. 19, 3239; 20, 3004; 21, 548, 1016, 2557; Ch. Soc. J. 55, 412, 610, etc.

Diazo-amido-benzene, $C_6H_5—N{=}N—NHC_6H_5$ (*Griess*).

Preparation. By adding $NaNO_2$ (1 mol.) to the solution of aniline (2 mols.) in HCl (3 mols.), and saturating with sodium acetate (B. 17, 641).

Properties. Bright yellow lustrous plates or prisms, insoluble in water but readily soluble in hot alcohol, ether and benzene. M. Pt. 98°. Far more stable than the diazo-compounds.

Isomers of the diazo-compounds, the **Nitrosamines of aromatic bases**, have just been discovered (Chemiker Zeitung for March, 1894):

$C_6H_5—N{=}N—OK$	$C_6H_5—NK—NO$
Potassium diazo-benzene (*Griess*).	Potassium phenyl-nitrosamine.

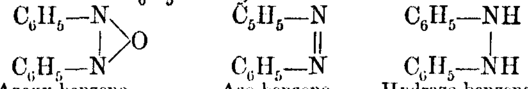
Potassium diazo-benzene, which—notwithstanding the doubts expressed by *Curtius*—possesses the normal formula assigned to it by *Griess*, and which is produced quantitatively, undergoes a molecular transformation into the isomeric potassium salt under the influence of concentrated alkali at 120°–130° (?); the latter crystallizes well, and may be distinguished from the former by the fact that it cannot yield azo-dyes with phenol, etc. With ethyl iodide it gives the nitrosamine of secondary ethyl-aniline. Acids cause it to change back again into the diazo-compound.

This formation of nitrosamine takes place even in the cold with *p*-*nitraniline, and the paste of the p-nitrophenyl-nitrosamine (which is a perfectly stable substance)* is now a valuable trade product. It only requires to be mixed with *β*-naphthol-alkali and imprinted on the cloth, and the latter then to be washed through acetic acid or merely exposed for a considerable time to the air, *i.e.* to the carbonic acid of the air, when the dye is produced in the fibre itself ("*Nitrosamine red*").

C. Azo-compounds.

While the reduction of nitro-compounds in acid solution leads to the aromatic amines, the use of alkaline reducing agents such as sodium amalgam, zinc dust and caustic soda, and also potash and alcohol, gives rise for the most part to intermediate products, the azoxy-, azo- and hydrazo-compounds.

$C_6H_5—NO_2$, Nitro-benzene.



Azoxy-benzene. Azo-benzene. Hydrazo-benzene.

$C_6H_5—NH_2$, Aniline.

Of these the azo-compounds are the most important.

1. Azoxy-compounds.

The azoxy-compounds are mostly yellow or red crystalline substances which result from the action of alcoholic potash, and especially of potassium methylate (B. **15**, 865), upon the nitro-compounds. Many of them may also be obtained by the oxidation of azo-compounds. They are of neutral reaction, and are very readily changed into azo-compounds, etc. upon reduction.

Azoxy-benzene, $(C_6H_5)_2N_2O$ (*Zinin*), forms pale yellow needles of M. Pt. 36°, insoluble in water but easily soluble in alcohol and ether. Concentrated sulphuric acid transforms it into the isomeric *p*-oxy-azo-benzene, $C_6H_5N{=}N{-}C_6H_4OH$.

2. Hydrazo-compounds.

The hydrazo-compounds are colourless, crystalline and of neutral reaction, and—like the azo-compounds—they cannot be volatilized without decomposition; for instance, hydrazo-benzene decomposes into azo-benzene and aniline when heated. They are obtained by the reduction of azo-compounds by sulphide of ammonium or zinc dust. Oxidizing agents such as ferric chloride readily transform them into azo-compounds, into which they also change slowly in the air alone. The stronger reducing agents, *e.g.* sodium amalgam, convert them into amido compounds.

Strong acids cause them to change into the isomeric derivatives of diphenyl (p. 476); thus from hydrazo-benzene and hydrochloric acid there results benzidine chloride (p. 477):

$$C_6H_5{-}NH{-}NH{-}C_6H_5 = \underbrace{NH_2{-}C_6H_4{-}C_6H_4{-}NH_2}_{\text{Benzidine.}}$$

This molecular rearrangement does not take place if the hydrogen which occupies the para-position to the imido-group is replaced by other groups. In such cases a partial rearrangement only occurs, and derivatives of diphenylamine are formed (B. **25**, 992, 1013, 1019); thus *p*-hydrazo-toluene,

$$\begin{array}{l} NH{-}C_6H_4.CH_3 \\ | \\ NH{-}C_6H_4.CH_3 \end{array}, \text{ yields } o\text{-amido-di-}p\text{-tolylamine}, \begin{array}{l} HN{-}C_6H_4.CH_3 \\ \quad\diagdown \\ H_2N{-}C_6H_3.CH_3. \end{array}$$

Hydrazo-benzene, $C_6H_5{-}NH{-}NH{-}C_6H_5$ (*Hofmann*), forms colourless plates of camphor-like odour, which are only slightly soluble in water, but readily soluble in alcohol and ether; M. Pt. 131°. The imido-hydrogen atoms are replaceable by acetyl- or nitroso-groups.

3. Azo-compounds.

The azo-compounds are red or yellowish-red crystalline indifferent substances insoluble in water but soluble in alcohol, some of them, *e.g.* azo-benzene, being capable of distillation

without change. Oxidizing agents convert them into azoxy-, and reducing agents into hydrazo- or amido-compounds. Chlorine and bromine act as substituents.

The so-called "mixed" azo-compounds, which contain a benzene radicle and an alcoholic radicle of the fatty series, are also known, *e.g.* **Azo-phenyl-ethyl**, $C_6H_5—N=N—C_2H_5$, a bright yellow oil.

Modes of formation. 1. By the cautious reduction of nitro- or azoxy-compounds, *e.g.* by means of sodium amalgam, an alkaline solution of stannous oxide (B. 18, 2912), etc.

2. By distilling azoxy-benzene with iron filings.

3. By the oxidation of hydrazo-benzene.

4. By the oxidation of amido-compounds, *e.g.* together with azoxy-compounds by means of $KMnO_4$:

$$2C_6H_5.NH_2 + O_2 = C_6H_5—N=N—C_6H_5 + 2H_2O.$$

5. By the action of nitroso- upon amido-compounds. In this way azo-benzene is obtained from nitroso-benzene and aniline acetate:

$$C_6H_5—NO + NH_2.C_6H_5 = C_6H_5—N=N—C_6H_5 + H_2O.$$

Azo-benzene,* $C_6H_5—N=N—C_6H_5$ (*Mitscherlich*, 1834), crystallizes in beautiful large red plates; M. Pt. 68°, B. Pt. 293°.

Azo-toluenes, $C_6H_4(CH_3)—N=N—C_6H_4(CH_3)$. All three are known.

4. Amido-azo- and Oxy-azo-compounds.

Amido-groups or hydroxyls are capable of entering into azo-benzene etc., whereby amido- and oxy-azo-benzenes are formed, thus:

$$\underbrace{C_6H_5—N=N—C_6H_4(NH_2)}_{\text{Amido-azo-benzene.}} \qquad \underbrace{C_6H_5—N=N—C_6H_4(OH).}_{\text{Oxy-azo-benzene.}}$$

The former are at the same time bases and azo-compounds, and the latter azo-compounds and phenols (*i.e.* weak acids, cf. p. 411).

Formation. 1. Amido-azo-benzene is obtained from azo-benzene by first nitrating it and then reducing the resulting mononitro-azo-benzene.

2. Oxy-azo-benzene results from azoxy-benzene by warming it with concentrated sulphuric acid, (cf. p. 401).

3. Amido-azo-compounds are also formed by the molecular rearrangement of the diazo-amido-compounds, according to p. 399, *i.e.* in a manner indirectly by the action of diazo-benzene etc. upon primary or secondary amines.

4. The corresponding amido-compounds, whose amido-hydrogen is substituted, result directly from the action of diazo-compounds upon tertiary amines (cf. p. 397).

The amido-group takes up here the para-position to the azo-group. But if this position is already occupied, a molecular transformation of diazo-amido into amido-azo-compounds becomes much more difficult, and the ortho-position is therefore taken up. The *o*-amido-compounds, thus produced, differ essentially from their isomers of the *p*-series.

With *m*-diamines, the diazo-compounds yield diamido-azo-benzenes:

$$C_6H_5.N{=}N.Cl + C_6H_4(NH_2)_2 = \underbrace{C_6H_5N{=}N-C_6H_3.(NH_2)_2}_{\text{Chrysoïdin.}} + HCl.$$

Oxy-azo-compounds result in an analogous manner by the action of diazo-compounds upon phenols in presence of alkali:

$$C_6H_5N{=}N.Cl + C_6H_5OK = C_6H_5N{=}N-C_6H_4OH + KCl.$$

Reactions of this kind take place especially with resorcin and the phenols of the naphthalene series (which see).

The amido- and oxy-azo-compounds are yellow, red or brown in colour and crystalline, and are mostly insoluble in water but moderately soluble in alcohol. They possess the character of dyes (azo-dyes), the chromogenic character of the azo-benzene being developed by the entrance of the salt-forming groups NH_2 etc. or of OH (cf. p. 32). Thus faintly acid solutions of amido-azo-benzene colour wool and silk a beautiful yellow ("**Aniline yellow**"), and **Chrysoïdin**, $C_{12}H_{12}N_4$, HCl, is an orange-red dye. To this class also belongs Vesuvine or Bismarck brown (see below).

Instead of these compounds themselves, their sulphonic acids (p. 408) are generally used as dyes; thus the so-called "**fast yellow**" ("*Echtgelb*") is the sodium salt of amido-azo-benzene-sulphonic acid.

The dyes which are derivatives of amido-azo-benzene are termed

Chrysoïdines, and those which are derivatives of oxy-azo-benzene, *Tropæolines*.

Of especial importance are those azo-dyes which contain a naphthalene radicle in the molecule. They are formed in a manner exactly analogous to the compounds mentioned above, the two naphthylamines, $C_{10}H_7.NH_2$, and the α- and β-naphthols, $C_{10}H_7.OH$, possessing respectively complete aminic and phenolic characters, and their sulphonic acids being very active chemically. They dye yellow, orange, red, brown, violet and even blue. Worthy of special mention is **Orange II.**, $C_6H_4(SO_3Na)-N=N-C_{10}H_6(OH)$, which is obtained from diazo-benzene-sulphonic acid and β-naphthol.

The amido-group in *p*-amido-azo-benzene may be diazotized, as given above, and the resulting diazo-compound is now capable—like diazo-benzene chloride—of yielding azo-compounds with amines or phenols, **Dis-azo- (tetrazo-) compounds**, as they are termed, (B. **15**, 25); *e.g.* $C_6H_5-N=N-C_6H_4-N=N-C_6H_4.OH$, (B. **9**, 628). Many of the most valuable azo-dyes, such as Biebrich scarlet, Croceïn scarlet etc. are derivatives of such diazo-compounds.

Tris-azo-compounds also exist, (B. **16**, 2028).

In the formation of azo-dyes of this nature, the azo-group always takes up the *para-position to the amidogen or hydroxyl* if possible. Should this be already occupied, it goes into the ortho-position. This point is elucidated by the examination of the decomposition products which result upon reduction. The azo-dyes are broken up at the point of the double bond by tin and hydrochloric acid and by sulphide of ammonium, two amido-compounds resulting, thus:

$$C_6H_5-N=N-C_6H_4N(CH_3)_2 + 2H_2 = C_6H_5NH_2 + C_6H_4(NH_2)-N(CH_3)_2.$$

The chemical nature of an azo-dye is thus often easily arrived at by investigating these decomposition products. Upon this reaction also depends the method of introducing new amido-groups into amines and phenols, mentioned on p. 383.

In place of the formulæ given above for amido- and oxy-azo-compounds, isomeric formulæ have also of late been taken into consideration (especially when the NH_2- or OH-group occupies the ortho-position to the azo-group); according to this the amido- and also the free oxy-azo-compounds appear as the hydrazones of quinones or quinone-imides. Oxy-azo-benzene would thus have the formula, $C_6H_5-NHN=C_6H_4=O$, but its potassium salt the (tautomeric) formula, $C_6H_5-N=N-C_6H_4-OK$. The behaviour of such compounds upon reduction favours this view (*H. Goldschmidt*, B. **24**, 2300; **25**, 1324; cf., on the other hand, B. **24**, 1592).

Amido-azo-benzene, *Aniline-yellow*, $C_6H_5-N=N-C_6H_4.NH_2$ (1863). Beautiful yellow plates or needles. The hydrochloric acid salt crystallizes in dark violet needles and yields a red solution.

Amido-azo-benzene-sulphonic acid (see p. 410) is prepared by sulphurating amido-azo-benzene, or by the combination of diazo-benzene-sulphonic acid with aniline:

$$C_6H_4(SO_3H)—N{=}N—Cl + C_6H_5NH_2$$
$$= C_6H_4(SO_3H)—N{=}N—C_6H_4—(NH_2) + HCl.$$

It has a flesh colour, its salts being yellow. The **Di-sulphonic acid** crystallizes in glittering violet needles and its salts are likewise yellow.

Dimethyl-amido-azo-benzene, $C_6H_5—N_2—C_6H_4.N(CH_3)_2$. Golden yellow plates. The chloride crystallizes in violet needles. Its **mono-sulphonic acid**, **methyl orange**, *helianthin*, or *Orange III.*, is used instead of litmus as a delicate indicator in alkalimetrical titrations, its yellow solution being coloured red by traces of acids; it is not affected either by CO_2 or H_2S, (B. **18**, 3290). It yields amido-dimethyl-aniline and sulphanilic acid upon reduction.

Diamido-azo-benzene, $C_6H_5—N{=}N—C_6H_3.(NH_2)_2$ (*Caro, Witt*, 1875); the chloride (*chrysoïdin*) crystallizes in large octahedra, built one upon the other.

Triamido-azo-benzene, $C_6H_4(NH_2)—N{=}N—C_6H_3(NH_2)_2$ (*Caro, Griess*, 1866), is produced by the action of N_2O_3 upon *m*-phenylene diamine, one half of the latter being partially diazotized to $C_6H_4(NH_2)—N{=}N.Cl$ and then acting on the other half, as given at p. 403. It forms brownish-yellow crystals, readily soluble in hot water; the salts are reddish-brown. Its hydrochloride, mixed with complex azo-substances, forms the colouring matter *Bismarck brown*, *Phenylene brown*, or *Vesuvine.*

Amido-azo toluene, from diazo-*p*-amido-toluene, has the constitution $C_6H_4(\overset{1}{C}H_3)—\overset{4}{N}{=}\overset{3}{N}—C_6H_3(\overset{1}{C}H_3)(\overset{4}{N}H_2)$, (B. **17**, 77). It crystallizes in orange-red needles. The alcoholic solution is turned green by hydrochloric acid.

Oxy-azo-benzene, $C_6H_5—N{=}\overset{1}{N}—C_6H_4(\overset{4}{O}H)$ (*Griess*, 1866), results from the action of diazo-benzene chloride upon phenol and also from the molecular transformation of azoxy-benzene, (cf. p. 401). It crystallizes in brick-red rhombic prisms and is a yellowish-red dye.

Dioxy-azo-benzene-sulphonic acid, $C_6H_4(SO_3H)—N=N—C_6H_3(OH)_2$, from diazo-benzene-sulphonic acid and resorcin, forms as sodium salt Chrysoïn or Tropaeolin O.

D. Hydrazines.

The hydrazines of the benzene series (*E. Fischer*) entirely correspond with those of the fatty, (cf. p. 128).

$C_6H_5—NH—NH_2$	$(C_6H_5)_2N—NH_2$	$(C_6H_5)(C_2H_5)N—NH_2$.
Phenyl-hydrazine.	Diphenyl-hydrazine.	Phenyl-ethyl-hydrazine.

Hydrazo-benzene results from the entrance of phenyl into the second amidogen of phenyl-hydrazine.

Phenyl-hydrazine, $C_6H_5—NH—NH_2$, forms a colourless crystalline mass, melting at 23° to a colourless oil which quickly becomes brown from oxidation, and which boils at 233° without decomposition. It combines with hydrochloric acid to the chloride, $C_6H_5N_2H_3$, HCl (plates). Like all hydrazines it is characterized by strong reducing power, reducing *Fehling's* solution even in the cold. It is readily destroyed by oxidation but is stable towards reducing agents; gentle oxidation of the sulphate by means of HgO converts it into diazo-benzene sulphate. Conversely, phenyl-hydrazine is *prepared:* (*a*) By reducing diazo-benzene chloride with the calculated quantity of $SnCl_2$ and HCl, (*V. Meyer* and *Lecco*, B. **16**, 2976):

$$C_6H_5—N=N.Cl + 2H_2 = C_6H_5—NH—NH_2, HCl.$$

(*b*) By reducing diazo-benzene potassium sulphite, $C_6H_5—N=N.SO_3K$ (from $C_6H_5N_2Cl$ and K_2SO_3), with zinc dust and acetic acid to phenyl-hydrazine potassium sulphite, $C_6H_5—NH—NH.SO_3K$, which is then broken up into phenyl-hydrazine and sulphuric acid upon heating with HCl:

$$C_6H_5—NH—NH—SO_3K + HCl + H_2O$$
$$= C_6H_5—NH—NH_2, HCl + SO_4KH.$$

By the action of halogen-alkyl upon phenyl-hydrazine, the imido-hydrogen atom of the latter is replaced by alkyl; the further action of halogen-alkyl gives rise at once to ammonium compounds, without replacement of the hydrogen of the amido-group. Acid radicles may replace either one or two H-atoms. In the first case Hydrazides are produced,—compounds which correspond to the amides, anilides, etc.; these give a violet-red colouration with sulphuric acid and bichromate of potash, and can be used for isolating acids which are readily soluble (B. **22**, 2728).

The base is an important and often an exceedingly delicate reagent for aldehydes and ketones, combining with them to hydrazones with elimination of water (cf. pp. 146 and 155; also B. **17**, 572; **21**, 984). Most of these compounds are solid and crystalline, and are therefore eminently suited for the recognition of aldehydes and ketones, and also of glucoses. Phenyl-hydrazine reacts in the first instance with the latter in the same way as it does with the former, but here (as also in the case of other aldehyde- and ketone-alcohols) a second hydrazine molecule may come into play, whereby osazones (p. 239) result. By the reduction of the hydrazones, primary amines are formed (B. **19**, 1924):

$$\underbrace{(CH_3)_2C{=}N{-}NH{-}C_6H_5}_{\text{Acetone-phenyl-hydrazone.}} + 2H_2 = \underbrace{(CH_3)_2CH.NH_2}_{\text{Iso-propylamine.}} + \underbrace{NH_2C_6H_5}_{\text{Aniline.}}$$

With aceto-acetic ether, phenyl-hydrazine forms pyrazole derivatives (see Antipyrine). It also reacts with lactones (B. **19**, 1706).

Phenyl-hydrazine hydrochloride is transformed into chloro-benzene by the action of hydrochloric acid in presence of sulphate of copper (B. **25**, 1074).

Phenyl-hydrazine-sulphonic acid (B. **18**, 2193). Is used for the preparation of tartrazine (p. 265).

Diphenyl-hydrazine, $(C_6H_5)_2N{-}NH_2$, is an oily base which boils without decomposition and, like phenyl-hydrazine, is easily oxidized; it only reduces *Fehling's* solution, however, when warmed. It is obtained by reducing diphenyl-nitrosamine, $(C_6H_5)_2N{-}NO$, with zinc dust and acetic acid. M. Pt. 34°. Like phenyl-hydrazine, it yields characteristic hydrazones with the sugars.

Acetyl-diphenyl-hydrazine results by a peculiar reaction from acetyl-phenyl-hydrazine and acetate of copper (B. **25**, 413).

Appendix. Phosphorus Compounds, etc.; Organo-metals.

The phosphorus- etc. compounds of the fatty series have their analogues in corresponding compounds of the aromatic, these latter having been investigated by *Michaelis* and his pupils (A. **181**, **188**, **201**, **212**, and **229**; B. **25**, 1747); for instance, **Phenyl-phosphine**, $C_6H_5.PH_2$; **Phenyl-phosphinic acid**, $C_6H_5PO(OH)_2$; **Phosphenyl chloride**, $C_6H_5.PCl_2$; **Phosphino-benzene**, $C_6H_5PO_2$; and **Phospho-benzene**, $C_6H_5P{=}P.C_6H_5$ (these two last being analogous to nitro- and to azo-benzene). Some of those compounds are solid, and they are less volatile and more stable than the corresponding aliphatic compounds.

Phosphenyl chloride is obtained, among other methods, by leading a mixture of benzene and phosphorus trichloride through a red-hot tube. It is a liquid of piercing odour; B. Pt. 225°.

We are also acquainted with phenyl compounds of boron, silicon, antimony, bismuth, tin, lead and mercury, *e.g.* mercury diphenyl (p. 362).

XXII. AROMATIC SULPHONIC ACIDS.

The aromatic sulphonic acids are very similar in properties to the sulphonic acids of the fatty series.

Benzene-sulphonic acid, $C_6H_5.SO_3H$ (*Mitscherlich*, 1834), results upon warming benzene with concentrated sulphuric acid (see p. 338):

$$C_6H_6 + SO_4H_2 = C_6H_5.SO_3H + H_2O.$$

As in the case of ethyl-sulphuric acid, advantage is taken of the solubility of its barium, calcium or lead salt to separate it from the excess of sulphuric acid; or its sodium salt is separated by the addition of sodium chloride. For its formation from diazo-benzene chloride, see p. **397**, and B. **23**, 1454.

Small tables ($+1\frac{1}{2}H_2O$), deliquescent in the air and readily soluble in alcohol. The barium salt crystallizes in glancing mother-of-pearl plates.

Behaviour. 1. Benzene-sulphonic acid is very stable, not being decomposed when boiled with alkalies or acids, as ethyl-sulphuric acid is. It is, however, broken up into benzene and sulphuric acid when heated with hydrochloric acid to 150°, or with water vapour at a high temperature (cf. p. 358):

$$C_6H_5.SO_3H + H_2O = C_6H_6 + SO_4H_2.$$

2. When fused with alkali, it yields phenol:

$$C_6H_5.SO_3K + KOH = C_6H_5.OH + SO_3K_2.$$

3. When it is distilled with potassium cyanide, benzo-nitrile is formed:

$$C_6H_5.SO_3K + CNK = C_6H_5.CN + SO_3K_2.$$

4. When it is acted upon by PCl_5, its chloride, **Benzene-sulphonic chloride,** results:

$$C_6H_5.SO_2OH + PCl_5 = C_6H_5.SO_2Cl + POCl_3 + HCl.$$

The latter is an oil, insoluble in water, M. Pt. 14·5°, B. Pt. 120° (under a pressure of 10 m.m. of mercury); as an acid chloride it is reconverted *into sulphonic acid by hot water, into the corresponding esters by alcohols,* and into **Benzene-sulphonamide,** $C_6H_5.SO_2.NH_2$ (lustrous mother-of-pearl sublimable plates), by ammonia. This compound can be sublimed, and corresponds with other amides in its properties. The amido-group, however, is so affected by the strongly acidifying action of the SO_2-group that its hydrogen is replaceable by metals, and the sulphone-amides consequently *dissolve in solutions of aqueous alkalies.*

Benzene-sulphonic chloride likewise yields sulphone-amides with primary *and secondary amines,* $C_6H_5.SO_2.NHR$ *and* $C_6H_5.SO_2.NRR'$, the former of these being soluble in alkali, but the latter insoluble. Tertiary amines do not of course give sulphone-amides. Upon this fact a good method for separating primary, secondary, and tertiary bases is founded (*Hinsberg,* B. **23**, 2962).

5. When benzene-sulphonic chloride is treated with zinc dust, benzene-sulphinate of zinc is formed:

$$2C_6H_5.SO_2Cl + 2Zn = (C_6H_5SO_2)_2Zn + ZnCl_2.$$

An alkaline sulphinate is also produced (along with phenyl disulphide as by-product) when benzene-sulphonic chloride is treated with thio-phenol in presence of alkali.

Benzene-sulphinic acid crystallizes in large glancing prisms, readily soluble in hot water, alcohol, and ether. It possesses reducing properties and is itself converted into thio-phenol by nascent hydrogen:

$$C_6H_5.SO_2H + 2H_2 = C_6H_5SH + 2H_2O.$$

The sulphone, **Sulpho-benzide,** $(C_6H_5)_2SO_2$, results from the action of SO_3 upon benzene, and also from the oxidation of phenyl sulphide, $(C_6H_5)_2S$. It crystallizes in plates, is only sparingly soluble in water

but more readily in alcohol, and distils unchanged. In properties it is analogous to diethyl-sulphone. Mixed sulphones are also known, *e.g.* **Phenyl-ethyl-sulphone**, $(C_6H_5)(C_2H_5)SO_2$.

Isomeric with the sulphones are the (easily decomposable) ethers of benzene-sulphinic acid, *e.g.* $C_6H_5.SO_2(C_2H_5)$; cf. B. 24, 1147.

Substitution may be effected in benzene-sulphonic acid by chlorine, bromine, and the groups NO_2 and NH_2.

The **Nitro-benzene-sulphonic acids**, $C_6H_4(NO_2).SO_3H$, result upon nitrating benzene-sulphonic acid or upon sulphurating nitro-benzene, the *m*-compound preponderating. Reduction converts them into the :

Amido-benzene-sulphonic acids, $C_6H_4(NH_2).SO_3H$. The *p*-compound, which is termed **Sulphanilic acid**, is obtained by heating aniline with fuming sulphuric acid, or from aniline sulphate at 180° to 200° (*Gerhardt*, 1845); also by reducing *p*-nitro-benzene-sulphonic acid. It forms rhombic plates $(+H_2O)$, rather difficultly soluble in water, which weather in the air.

It combines with bases, *e.g.* with soda to sodium sulphanilate, $C_6H_4NH_2SO_3Na + 2H_2O$ (large plates), but not with acids. The formula $C_6H_4\!<\!\genfrac{}{}{0pt}{}{NH_3}{SO_3}\!>$ possibly expresses the constitution of sulphanilic acid. The *m*-acid, also termed **Metanilic acid**, is employed in the preparation of azo-dyes; *e.g.* metaniline yellow; it crystallizes in fine needles or prisms.

Diazo-benzene-sulphonic acid, $C_6H_4\!<\!\genfrac{}{}{0pt}{}{N=N}{SO_3}\!>$ (the anhydride of $C_6H_4\!<\!\genfrac{}{}{0pt}{}{N=N.OH}{SO_3H}$), is obtained by adding a mixture of sulphanilate and nitrite of sodium to dilute sulphuric acid. White needles, sparingly soluble in water. It shows all the reactions of the diazo-compounds and is of great importance for the preparation of azo-dyes (p. 403).

Benzene-disulphonic acids, $C_6H_4(SO_3H)_2$ (principally meta-), and **Benzene-trisulphonic acids**, $C_6H_3(SO_3H)_3$, result from the energetic sulphuration of benzene. The former exist, of course, in three isomeric modifications. When they are distilled with KCN, they yield the compounds $C_6H_4(CN)_2$, the nitriles of the phthalic acids; when fused with KOH, the *m*-disulphonic acid changes into resorcin (*m*-dioxy-benzene), $C_6H_4(OH)_2$.

A Di-sulphanilic acid, $C_6H_3(NH_2)(SO_3H)_2$, has also been prepared.

Almost all the homologues of benzene, with the exception of hexamethyl-, etc., benzene, are likewise capable of yielding sulphonic acids. From toluene are obtained the **Toluene-sulphonic acids**, $C_6H_4(CH_3)SO_3H$, which—as di-derivatives—exist in three different modifications. Of these it is the *p*-acid which is formed in largest quantity directly; its potassium salt crystallizes beautifully.

The sulphonic acids of the three xylenes, the **Xylene-sulphonic acids**, $C_6H_3(CH_3)_2SO_3H$, serve for the separation of these isomers from each other; and the power of crystallization of the salts or amides of the sulphonic acids of the higher benzene homologues is frequently made *use of for the recognition and separation of these hydrocarbons.*

As an example of a complicated aromatic sulphonic acid may be mentioned *o*-**Bromo**-*m*-**nitro**-*p*-**toluene-sulphonic acid**, $C_6H_2(CH_3)Br(NO_2)(SO_3H)$.

The above instance is sufficient to show that sulphonic acids may be obtained from the most complicated aromatic compounds. This is of especial importance if the latter are dyes whose application is hindered by their insolubility in water or by other circumstances, as in the case *e.g.* of indigo, amido-azo-benzene, etc.; it is true that the sulphonated dyes are usually inferior to their originals in colouring power and purity, *e.g.* they do not stand the effects of light so well (indigo, for example).

For sulphonic acids of the azo-dyes, see p. 404.

XXIII. PHENOLS.

Phenols are oxygenated derivatives of benzene which stand midway in chemical character between alcohols and acids. They are derived from the benzene hydrocarbons in the same way as the alcohols of the fatty series are from the paraffins, *i.e.* by the replacement of hydrogen in the benzene nucleus by hydroxyl.

The phenols are either liquid or solid compounds and are often characterized by a peculiar odour, *e.g.* carbolic acid and thymol. Most of them can be distilled without decomposition and are readily soluble in alcohol and ether; some dissolve easily in water, others with more difficulty. Many of them are antiseptics, *e.g.* phenol, creosol and resorcin.

Summary of the most important Phenols.

Monatomic :	Diatomic :	Triatomic :
$C_6H_5.OH$ Phenol [42°] (181°)	$C_6H_4(OH)_2$ Dioxy-benzenes	$C_6H_3(OH)_3$ Trioxy-benzenes *v* = Pyrogallol [115°] (2 *a* = Oxy-hydroquinone *s* = Phloroglucin (217°)
$C_6H_4(CH_3).OH$ Cresols *o-* : *m-* : *p-* : 31°] (188°) [3°] (201°) [36°] (198°)	*o* = Pyrocatechin [104°] (245°) *m* = Resorcin [118°] (280°) *p* = Hydroquinone [169°] [$C_6H_4O_2$ Quinone]	$C_6H_2(CH_3)(OH)_3$ Methyl-pyrogallol
$C_6H_3(CH_3)_2.OH$ Xylenols *e.g.* [74°] (211°)	$C_6H_3(CH_3)(OH)_2$ 1:3:5 = Orcin [107°] (288°) 1:3:4 = Homo-pyro-catechin	**Tetratomic :** $C_6H_2(OH)_4$ Tetroxy-benzene
C_9, ψ-Cumenols		
C_{10}, Durenols $C_6H_3(CH_3)(C_3H_7).OH$ Thymol [51°] (222°) Carvacrol [0°] (237°)	C_8, Xylorcin, etc.	**Hexatomic :** $C_6(OH)_6$ Hexoxy-benzene
C_{11}, Penta-methyl-phenol	C_9, Mesorcin	

Behaviour. 1. The phenols behave like alcohols in that they are capable of forming ethers such as anisol, $C_6H_5.O.CH_3$, saponifiable ethers such as phenyl-sulphuric acid, $C_6H_5.O.SO_3H$, thio-compounds, etc.

They can only be compared with the tertiary alcohols, since they cannot, like the primary or secondary, yield acids or ketones containing an equal number of carbon atoms in the molecule upon oxidation.

Unlike the alcohols, however, the phenols are very stable as regards oxidizing agents, undergoing only substitution and not oxidation by halogens and nitric acid, and not going into hydrocarbons with elimination of water, etc.

2. The phenols possess the character of weak acids; they form salts with alkalies, etc., most of which are readily soluble in water, and which correspond with the alcoholates but are far more stable than these. Thus, the phenols dissolve in the alkalies to salts; the latter are usually decomposed,

however, by carbonic acid. The acid character of the phenols is considerably increased by the entrance of negative groups, especially NO_2, into the molecule. (See picric acid.)

3. The phenols are true derivatives of benzene. They are capable of yielding all those varieties of derivatives which have been described as derivatives of benzene, *e.g.* chloro-, bromo-, nitro-, amido-, diazo- and sulpho-phenols. The ease with which chlorine, bromine, nitric acid, etc., produce such derivatives is characteristic of the phenols; thus the former substitute even in very dilute aqueous solution, and nitrophenols also result from the action of dilute HNO_3, the concentrated acid giving rise at the same time to di- and trinitro-compounds.

From the phenols having the character of weak acids, it follows that *the group* C_6H_5 (phenyl) *is of a negative nature, i.e. that it acts as an* acid radicle.

Occurrence. Many individual phenols are found in the vegetable and animal kingdoms.

Constitution. The hydroxyl in phenol, $C_6H_5.OH$, and in the dioxy- and trioxy-benzenes, etc., containing six carbon atoms, is linked to the benzene nucleus. That this is also the case in the homologues of those compounds follows: (*a*) from their completely analogous reactions; (*b*) from their behaviour upon oxidation. The products which hereby result from the transformation of the side chains into carboxyl are oxy-acids, *i.e.*, still contain the hydroxyl.

The entrance of the hydroxyl into the side chain of the benzene homologues is also theoretically possible, but in this case it is not phenols which result but true aromatic alcohols, (cf. p. 431)

A. Monatomic Phenols.

Modes of formation. 1. Many phenols result from the destructive distillation of the more complex carbon compounds, especially of wood and coal; they are therefore present in wood and coal tars. The latter contains especially

phenol and its homologues, cresol, etc.; the former, among other products, the methyl ethers of polyatomic phenols, *e.g.* guaiacol, $C_6H_4.(OH)(O.CH_3)$, and its homologue creosol, $C_6H_3.CH_3(OH)(O.CH_3)$.

The phenols are isolated from coal tar etc. by shaking up with potash, in which they dissolve, saturating the solution with hydrochloric acid, and purifying the precipitated phenols by fractional distillation.

2. The phenols result together with a sulphite upon fusion of the sulphonic acids with potash or soda, (*Kekulé*, *Wurtz*, *Dusart*, 1867):

$$C_6H_5.SO_3K + 2KOH = C_6H_5.OK + SO_3K_2 + H_2O.$$

In the laboratory nickel or silver basins are used for this fusion, and on the large scale iron boilers, etc. The chlorinated sulphonic acids and the chlorinated phenols also exchange the halogen for hydroxyl upon fusion with potash:

$$C_6H_4.Cl(SO_3K) + 4KOH = C_6H_4(OK)_2 + SO_3K_2 + KCl + 2H_2O.$$

3. By boiling the diazo-compounds with water (*Griess*; cf. p. 396). In this case a very dilute sulphuric acid solution is employed:

$$C_6H_4Cl(N:N.Cl) + H_2O = C_6H_4Cl(OH) + N_2 + HCl.$$

4. Phenol is produced from benzene by the action of ozone or hydrogen peroxide, and also by that of the oxygen of the air in presence of caustic soda solution or of aluminium chloride. In an analogous manner di- and even tri-oxy-benzene may be obtained by fusing phenol with potash:

$$C_6H_5.OH + O = C_6H_4(OH)_2.$$

5. The phenols cannot be prepared from chloro-, bromo- or iodobenzene as the alcohols can from chloro-, bromo- or iodo-alkyl, the halogen being bound too firmly to the benzene nucleus. If, however, nitro-groups are present at the same time, an exchange of this kind can be effected by heating with potash or soda solution; trinitrochloro-benzene indeed reacts with water alone:

$$C_6H_2Cl.(NO_2)_3 + HOH = C_6H_2(OH)(NO_2)_3 + HCl.$$

6. Similarly the amido-group in amido-compounds may be replaced by hydroxyl upon boiling with alkalies, provided nitro-groups are

also present; thus *o*- and *p*- (not *m*-) dinitro-aniline yield dinitrophenols, a reaction which corresponds with the saponification of the amides, (cf. pp. 350–351).

7. Phenols result from the dry distillation of the salts of the aromatic oxy-acids with lime, or from that of their silver salts, *e.g.*

$$C_6H_2(OH)_3.CO_2H = CO_2 + C_6H_3(OH)_3.$$

Gallic acid. Pyrogallol.

8. Homologues of the phenols are produced by heating phenol with alcohols and zinc chloride, *e.g.* ethyl and butyl phenols, (B. **14**, 1845; **15**, 150).

9. Phenols also result from the putrefaction of albumen, especially *p*-cresol, $C_6H_4(CH_3)OH$.

Behaviour. 1, 2, and 3. For the alcoholic and acid characters of the phenols and for their substitution, see above and also on p. 417 *et seq.* Bromine water precipitates even very dilute aqueous solutions of phenol, with the formation of tribromophenol.

4. Many phenols give characteristic colourations with ferric chloride in neutral solution, *e.g.* phenol and resorcin violet, pyro-catechin green, and orcin blue-violet; while pyrogallol yields a blue colour with ferrous sulphate containing a ferric salt, and a red one with ferric chloride. Chloride of lime and iodine also sometimes give particular colourations.

5. When the phenols are mixed with concentrated H_2SO_4 and some $NaNO_2$, they yield intensely coloured solutions which turn to king's blue on saturation with potash, (the *Liebermann* reaction, p. 387).

6. The sodium and potassium salts of the phenols react with CO_2 (*Kolbe*) or with $COCl_2$, with formation of aromatic oxy-acids, *e.g.* salicylic acid:

$$C_6H_5.OH + CO_2 = C_6H_4(OH).CO_2H.$$

The oxy-acids are also formed when CCl_4 and NaOH are used, (B. **9**, 1285), and their aldehydes by the action of $CHCl_3$ and NaOH upon phenol, (B. **9**, 824).

7. The phenols combine with diazo-compounds to form azo-dyes (p. 403); when heated with benzo-trichloride, $C_6H_5.C{\equiv}Cl_3$, they yield yellow-red dyes (see aurin), and with phthalic acid, the phthaleïns.

8. When heated with zinc dust, the phenols are converted into the corresponding hydrocarbons (*Baeyer*):

$$C_6H_5.OH + H_2 = C_6H_6 + H_2O.$$

9. Upon heating with zinc or calcium chloride and ammonia, the OH is replaced by NH_2 (cf. p. 377; also B. **19**, 2901).

10. Heating with PCl_5 partially converts the phenols into chlorinated hydrocarbons, and heating with P_2S_5 into thio-phenols (p. 418).

11. For the breaking up of the phenols by chlorine, see p. 355.

12. For the oxidation of phenol by permanganate of potash to *i*-tartaric acid, see B. **24**, 1753.

Phenol.

Phenol, *carbolic acid, phenyl alcohol,* C_6H_5OH. Discovered in 1834 by *Runge* in coal tar. Occurs in the urine of the herbivora and in human urine as phenyl-sulphuric acid, in castoreum and in bone oil. It forms a colourless crystalline mass consisting of long needles. M. Pt. 42°; B. Pt. 181°; Sp. Gr. at 0°, 1·084. It is soluble in 15 parts of water at 16°, and itself dissolves some water, a small percentage of the latter sufficing to liquify the crystalline phenol; alcohol and ether dissolve it readily. It is hygroscopic and acquires a reddish colour in the air, possesses a characteristic odour and burning taste, is poisonous, and acts as a splendid antiseptic. It exerts a strongly corrosive action upon the skin. Soluble in caustic potash but not in the carbonate. Ferric chloride colours the aqueous solution violet, while a pine shaving moistened with hydrochloric acid is turned greenish-blue by phenol.

Phenol-potassium, $C_6H_5.OK$, results upon heating phenol with KOH. It crystallizes in white needles which are readily soluble in water and which redden in the air.

Phenol-calcium or carbolate of lime, $(C_6H_5.O)_2Ca$, is employed as a disinfectant. The corresponding **Mercury** compound, $(C_6H_5.O)_2Hg$, which crystallizes in colourless needles, is used in skin diseases.

For the *reactions* of phenol and its homologues, see B. **14**, 2306; **15**, 1207.

Hexa-hydro-phenol, $C_6H_5.H_6.OH$, prepared from quinitol as given in B. **26**, 229, is a liquid with an odour resembling that of fusel oil.

Summary of the most important derivatives of Phenol.

Substitution Products.	Ethers.	*Compound ethers.*
$C_6H_4(OH)Cl$ (3) Chloro-phenols. *p*- : [37°] (217°)	$C_6H_5.O(CH_3)$ Anisol. Liq. (155°)	$C_6H_5.O(SO_3H)$ Phenyl-sulphuric acid.
$C_6H_4(OH).NO_2$ (3) Nitro-phenols. *o*- : [45°] (214°) ; *p*- : [114°]	$C_6H_5.O(C_2H_5)$ Phenetol. Liq. (172°)	$C_6H_5.O(C_2H_3O)$ Acetyl-phenol. (193°)
$C_6H_2(OH)(NO_2)_3$ Trinitro-phenols. [*e.g.* 123°]	$C_6H_5.O.C_6H_5$ Diphenylether. [28°](253°)	—— Thio-compounds.
$C_6H_4(OH).NH_2$ (3) Amido-phenols. *o*- : [170°] ; *p*- : [184°]	$C_6H_4(NH_2).OCH_3$ (3) Anisidines. *p*- : [56°] (245°)	$C_6H_5.SH$ Thio-phenol. (172°)
$C_6H_4(OH).SO_3H$ (3) Phenol-sulphonic acids.	$C_6H_3(NH_2)(OCH_3)(SO_3H)$ Anisidine-sulphonic acid.	$(C_6H_5)_2S$ Phenyl sulphide. (272°)

Ethers.

Anisol* or *phenyl-methyl ether*, $C_6H_5.O(CH_3)$, and **Phenetol** or *phenyl-ethyl ether*, $C_6H_5.O(C_2H_5)$, are best got by heating phenol-potassium (or phenol and caustic potash) with methyl or ethyl iodide in alcoholic solution :

$$C_6H_5.OK + CH_3I = C_6H_5.O(CH_3) + KI;$$

the former is also obtained by distilling anisic acid with lime. They are liquids of ethereal odour which boil at a lower temperature than phenol, just as ether boils at a lower one than alcohol. As regards behaviour, they are very stable neutral compounds of hydrocarbon character; when heated with HI to 140°, or with HCl to a higher temperature, or with aluminium chloride, they are decomposed backwards, thus:

$$C_6H_5.O.CH_3 + HCl = C_6H_5.OH + CH_3Cl.$$

This reaction serves for the quantitative determination of the number of methoxy-groups ($-O.CH_3$), in phenolic ethers (cf. *e.g.* B. **22**, Ref. 710).

Phenyl ether, *di-phenyl oxide*, $(C_6H_5)_2O$, is formed upon heating phenol with $ZnCl_2$ or Al_2Cl_6, but not with H_2SO_4. Long needles. Not split up by HI.

* Benzene-oxy-methane.

Compound ethers of Phenol.

Phenol reacts as an alcohol with inorganic and organic acids to form compound ethers.

Phenyl-sulphuric acid (also termed *phenol-sulphuric acid*), $C_6H_5.O(SO_3H)$, is only capable of existence in the form of salts, being immediately saponified into phenol and sulphuric acid when attempts are made to isolate it. The potassium salt, $C_6H_5.O.(SO_3K)$ (plates, sparingly soluble in water), is found in the urine of the herbivora and also in human urine after the consumption of phenol, and it may be prepared synthetically by heating phenol-potassium with potassic pyrosulphate in aqueous solution, (*Baumann*). It is very stable towards alkalies, but is saponified by hydrochloric acid.

The other phenol-sulphuric acids, *e.g.* cresol-sulphuric acid, which occur in urine, are exactly analogous to the above.

Phenol-carbonic ether, *phenyl carbonate*, $CO(O.C_6H_5)_2$, is prepared from $COCl_2$ and C_6H_5ONa. It crystallizes in glancing needles, M. Pt. 78°, and is convertible into salicylic acid.

Sodium phenyl-carbonate, $C_6H_5.O.CO_2Na$, results from CO_2 and $C_6H_5.ONa$, and goes into sodium salicylate upon heating. Acids decompose it into CO_2 and phenol.

Acetyl-phenol, $C_6H_5O.C_2H_3O$, obtained from phenol-sodium and acetyl chloride, or from phenol, acetic acid and sodium acetate, is an easily saponifiable liquid which boils at 193°.

Thio-phenols.

Thio-phenol, *phenyl hydrosulphide*, $C_6H_5.SH$, is prepared from benzene-sulphonic chloride, $C_6H_5—SO_2Cl$, as given at p. 409, or by heating phenol with P_2S_5; also by the exchange (best effected indirectly) of the diazo-group in diazo-benzene chloride for —SH (see B. 23, 738, Ref. 327). It is a liquid of most unpleasant odour and of pronounced mercaptan character (see p. 104).

It yields, for instance, a mercury compound, $(C_6H_5S)_2Hg$, crystallizing in glancing needles, and also salts with other metals. When warmed with concentrated H_2SO_4, a cherry-red and then a blue colouration is produced. It is readily oxidizable to phenyl disulphide.

Closely related to the above are (*a*) **Phenyl sulphide**, $(C_6H_5)_2S$, which results, among other methods, by the action of diazo-benzene chloride upon thio-phenol (B. **23**, 2469):—

$$C_6H_5—N{=}N—Cl + H—S—C_6H_5 = C_6H_5—S—C_6H_5 + N_2 + HCl.$$

It is a liquid smelling of leeks and is oxidizable to **Phenyl sulphone**, $(C_6H_5)_2SO_2$; (*b*) **Phenyl disulphide**, $(C_6H_5)_2S_2$ (glancing needles, M. Pt. 60°), which is very easily prepared by the action of iodine upon the potassium compound of thio-phenol, or by exposing an ammoniacal solution of the latter to the air. It is readily reducible to thio-phenol, and is indirectly oxidizable to **Benzene di-sulph-oxide**, $(C_6H_5)_2S_2O_2$. (Cf. the corresponding compounds of the fatty series, p. 102 *et seq.*)

Chloro- and Bromo-phenols.

When chlorine is led into phenol, *o*- and *p*-**Chloro-phenols** are formed. These also result, together with the *m*-compound, by reducing and diazotizing the haloid-nitro-benzenes.

Of the isomeric bi-derivatives, the *p*-compounds have the highest melting point and the *o*- the lowest; thus *o*-chloro- and bromo-phenols are liquid and the *p*-compounds solid. When fused with caustic potash they yield dioxy-benzenes (p. 423), often with a molecular rearrangement. The chloro-phenols have a sharp persistent odour. All the five hydrogen atoms of phenol have been replaced by chlorine and bromine.

Nitroso-phenols.

Nitroso-phenol, $C_6H_5O_2N$, is prepared from phenol and nitrous acid (*Baeyer*, B. **7**, 964), by boiling nitroso-dimethyl-aniline with caustic soda solution (see p. 388), and by the action of hydroxylamine upon quinone (p. 427). It crystallizes in fine colourless needles which readily become brown, or in large greenish-brown plates, and detonates when heated.

It yields a soda salt crystallizing in red needles and amorphous dark-coloured salts with the heavy metals. Potassic ferricyanide in alkaline solution oxidizes it to *p*-nitro-phenol, while tin and hydrochloric acid reduce it to *p*-amido-phenol. It gives the *Liebermann* reaction with phenol and concentrated sulphuric acid.

It was formerly given the formula $C_6H_4(NO)(OH)$, but is really an *iso-nitroso*-compound, an oxime of quinone, with the formula

$$C_6H_4\lt^{N.OH}_{O} \quad \text{or} \quad C_6H_4\lll^{N.OH}_{O}$$

(see Quinone; also B. **17**, 213, 801). This follows from its formation from quinone, and also from the fact that hydroxylamine converts it into quinone-dioxime (p. 429).

Nitro-phenols.

On mixing phenol with cold dilute nitric acid, *o*- and *p*-nitro-phenols are formed, the latter preponderating if the liquid is cold, and the former if it is warm. Upon distilling with steam, the 1 : 2 compound (strongly smelling yellow prisms) volatilizes, while the 1 : 4 (colourless tables) remains behind. For their formation, see also pp. 414 and 387. *m*-**Nitro-phenol** results from *m*-nitraniline by diazotizing the latter.

The acid character of phenol is so strengthened by the entrance of the nitro-group that its salts are not decomposed by CO_2 but result from the nitro-phenols and alkaline carbonate. *o*-**Nitro-phenol-sodium,** $C_6H_4(NO_2)ONa$, crystallizes in dark red prisms, and *p*-**Nitro-phenol-potassium** in golden needles. Halogens and nitric acid readily substitute further in these (or in phenol itself), yielding two isomeric **Dinitro-phenols,** $C_6H_3(NO_2)_2OH$, ($OH : NO_2 : NO_2 = 1 : 2 : 4$ and $1 : 2 : 6$, *i.e.* the two NO_2-groups are always in the *m*-position to one another). Further nitration gives:

Picric acid, *trinitro-phenol,* $C_6H_2(NO_2)_3.OH$, ($OH : NO_2 : NO_2 : NO_2 = 1 : 2 : 4 : 6$). This compound was discovered in 1799. It may also be prepared by the direct oxidation of *s*-trinitro-benzene with K_3FeCy_6, and is produced by the action of concentrated nitric acid upon the most various organic substances, *e.g.* silk, leather, wool, resins and aniline. It is a strong acid and forms beautifully crystallizing salts which explode violently upon heating or when struck. Very sparingly soluble in water. Crystallizes from alcohol or water in yellow plates or prisms, M. Pt. 122°. Can be sublimed without decomposition, but is explosive also. It is used for the preparation of explosives, and is also an important yellow dye.

Picryl chloride, $C_6H_2(NO_2)_3Cl$ (from picric acid and PCl_5), resembles the acid chlorides (p. 350) in behaviour. Picric acid forms beautifully crystallizing addition-compounds with many hydrocarbons, *e.g.* C_6H_6, $C_{10}H_8$, etc. With KCN it yields Iso-purpuric acid, $C_8H_5N_5O_6$, whose potassium salt dyes a garnet-brown like orchilla.

Isomers of picric acid are also known.

Amido-phenols.

The nitro-phenols go into amido-phenols upon reduction:

$C_6H_4(OH)NH_2$	$C_6H_3(OH)(NH_2)_2$	$C_6H_3(OH)NO_2(NH_2)$	$C_6H_2(OH)(NH_2)_3$.
o-, *m*-, *p*- Amido-phenols.	Di-amido-phenols.	Nitro-amido-phenols.	Tri-amido-phenol.

In the *Amido-phenols* (*Hofmann*, 1857) the acid character of the phenols is neutralized by the presence of the amido-groups, so that they only yield salts with acids; but, as phenols, they are still capable of yielding derivatives (see anisidine), while on the other hand their amido-hydrogen is exchangeable in the most various ways, as in the case of aniline, but chiefly for acid radicles.

The **Hydrochlorides** of the amido-phenols are relatively stable in the air, and are often capable of being sublimed; the free bases (colourless plates) on the other hand, especially if they are impure, are very readily oxidized in the air, with blackening and the formation of resin.

o-**Amido-phenol**, $C_6H_4(OH)(NH_2)$, M. Pt. 170°, yields with acids (like an *o*-diamine) so-called "anhydro-bases" instead of normal derivatives, *e.g.* with formic acid the compound **Methenyl-*o*-amido-phenol**, $C_6H_4<^{N}_{O}>CH$. *This last is crystalline and boils without decomposition.*

p-**Amido-phenol**, M. Pt. 184°, is easily oxidized to quinone, $C_6H_4O_2$, and is converted by chloride of lime into quinone chlor-imide, $C_6H_4O(NCl)$ (which see).

m-**Amido-phenol**, and **Diethyl-*m*-Amido-phenol**, $C_6H_4(OH)[N(C_2H_5)_2]$, result upon fusing *m*-amido-benzene-sulphonic acid or its diethyl derivative with alkali. Diethyl-*m*-amido-phenol is used for the preparation of the red dye *Rhodamine.*

Amido-thio-phenols, $C_6H_4(SH)NH_2$, are also known, of which the *o*-compound is again characterized by the ready formation of anhydro-compounds, such as **Methenyl-amido-thio-phenol**, $C_6H_4<^{N}_{S}>CH$, isomeric with phenyl isothiocyanate (*Hofmann*, B. **13**, 1226).

The yellow cotton dye, **Primuline**, a more complex compound of this nature, is obtained by heating *p*-toluidine with sulphur and then sulphurating the product.

The **Anisidines**, *amido-anisols*, *methoxy-anilines*, $C_6H_4(O.CH_3).NH_2$, and the **Phenetidines**, $C_6H_4(O.C_2H_5).NH_2$, are bases similar to aniline, and are used in the colour industry (azo-dyes).

Aceto-*p*-phenetidine, $C_6H_4(O.C_2H_5).(NH.C_2H_3O)$, which forms colourless crystals, is used as an anti-pyretic and a remedy for neuralgia, under the name of "*Phenacetine.*"

The **Oxy-diphenylamines**, *e.g.* $C_6H_5—NH—C_6H_4.OH$, are phenylated amido-phenols, and react accordingly (see also p. 389).

Salts of diamido-phenol 1:2:4 are used under the name of *Amidols* as photographic developers.

Phenol-sulphonic Acids.

Phenol-sulphonic acids, $C_6H_4(OH)(SO_3H)$. The *o*- and *p*-acids are obtained from phenol and concentrated H_2SO_4 at a moderate temperature, that is, with much greater ease than the benzene-sulphonic acids; the ortho-acid changes into the para- on warming, even when in aqueous solution. The *m*-compound can be prepared indirectly by fusing *m*-benzene-disulphonic acid with potash. All three are crystalline.

The *o*- and *m*-acids yield *o*- and *m*-dioxy-benzenes when fused with KOH, but the *p*-acid does not react in this way, being attacked only at temperatures over 320°, and no resorcin then resulting; the same applies to caustic soda. *o*-Phenol-sulphonic acid is used as an antiseptic under the name of "Aseptol" or "*Sozolic acid*" (B. 18, Ref. 506); similarly, **Di-iodo-*p*-phenol-sulphonic acid,** $C_6H_2.I_2(OH)(SO_3H)$, is "*Sozo-iodol*," an antiseptic like iodoform.

Phenol-di- and tri-sulphonic acids are also known.

Homologues of Phenol.

The homologues of phenol resemble the latter very closely in most of their properties, form perfectly analogous derivatives, and possess likewise a disinfectant action and a peculiar odour (the cresols an unpleasant fæcal-like odour, the higher homologues one which is less marked).

They differ from phenol mainly by the presence of side chains which, as in the case of toluene etc., may undergo certain transformations. In especial, when they are used in the form of alkyl or acetyl derivatives or sulphonic acids, they can be oxidized in such a manner that the side chains (methyl groups) are transformed into carboxyl, with the production of oxy-carboxylic acids. The cresols themselves *cannot* be oxidized even by chromic acid mixture, but are completely destroyed by permanganate of potash.

Negative substituents, especially if they are present in the *o*-position, render such oxidation more difficult in acid, but facilitate it in alkaline solution.

The Cresols, $C_6H_4(CH_3)OH$, are all three present in coal

tar and are also contained in the tar from pine and beech wood; *they can be prepared from the corresponding toluidines.* *o*-Cresyl-sulphuric acid (analogous to phenyl sulphuric acid) is found in the urine of horses, and the *p*-compound in human urine.

m-Cresol is conveniently prepared by heating thymol with phosphoric anhydride and then with potash.

***p*-Cresol**, $C_6H_4(CH_3)OH$, is produced by the decay of albumen. Its dinitro-compound is a golden-yellow dye which is used as ammonium or potassium salt under the name of **Victoria orange.**

Crude cresol is rendered soluble in water by the addition of resin soap or of oil soap; the preparations so obtained are termed *Creoline* and *Lysol*, and are employed as antiseptics.

Thymol, $C_{10}H_{14}O$, (CH_3:C_3H_7:OH = 1:4:3) is found together with cymene, $C_{10}H_{14}$, and thymene, $C_{10}H_{16}$, in oil of thyme, Thymus Serpyllum, and is used as an antiseptic.

***m*-Xylenol**, $C_8H_{10}O$, (CH_3 : CH_3 : OH = 1 : 3 : 4) is found in the creosote of beech-wood tar.

Carvacrol, $C_{10}H_{14}O$, (CH_3 : C_3H_7 : OH = 1 : 4 : 2) present in Origanum hirtum, is prepared either by heating camphor with iodine or from its isomer, carvol, and vitreous phosphoric acid. **Carvol**, $C_{10}H_{14}O$, the chief constituent of oil of cumin (from Carvum Carvi), appears to be a keto-dihydrocymol (B. **19**, 12; **24**, 3985), since it yields carvoxime with hydroxylamine. Carvoxime, like carvol, exists in three optically different modifications.

For other **homologues** of phenol, see table, p. 412; **Ethyl-**, **Propyl-** and **Butyl-phenols** and also **Penta-methyl-phenol** (B. **18**, 1825) have likewise been prepared.

B. Diatomic Phenols.

By the entrance of two hydroxyls into benzene and its homologues, the diatomic phenols are produced. These are analogous to the monatomic compounds in most of their relations, but differ from them in the same way as the diatomic alcohols do from the monatomic. They are likewise formed by methods completely analogous to those for the monatomic phenols, especially by fusion with potash (p. 414); instead, however, of the compound expected, an isomeride which is stable at that high temperature frequently results (see Resorcin). The *p*-dioxy-compounds are characterized by their close connection with the quinones. *Many of the polyatomic phenols are strong reducing agents.*

(*a.*) *Dioxy-benzenes.* **Pyrocatechin**, $C_6H_4(OH)_2$ (1:2), **which was first obtained by the distillation of catechin (Mimosa Catechu),**

is present in raw beet sugar and results from the fusion of many of the resins as well as of *o*-phenol-sulphonic acid with potash. It crystallizes in short white rhombic prisms, which can be sublimed, and are readily soluble in water, alcohol and ether.

It is prepared by heating its mono-methyl ether, **Guaiacol**, $C_6H_4(OH)(O.CH_3)$, a constituent of beech-wood tar, with hydriodic acid (see Anisol, p. 417). Like most of the polyatomic phenols it is very unstable in an alkaline solution, which quickly becomes green and then black in the air. The aqueous solution is coloured green by Fe_2Cl_6 and then violet by NH_3 (reactions of the *o*-dioxy-compounds). It possesses reducing properties, causing separation of the metal from a solution of silver nitrate even in the cold. By the continued action of chlorine upon it, derivatives of penta-methylene and finally of the fatty series result (*Zincke* and *Küster*). By boiling it with potash and potassic methyl-sulphate, it may be reconverted into guaiacol, which likewise shows the ferric chloride reaction and possesses reducing powers. Guaiacol is employed medicinally as an expectorant. **Veratrol**, $C_6H_4(OCH_3)_2$, is its di-methyl ether.

Resorcin, $C_6H_4(OH)_2$, (1:3) (*Hlasiwetz*, *Barth*, 1864), is obtained on fusing many resins (Galbanum, Asafœtida), also *m*-phenol-sulphonic acid, all three bromo-benzene-sulphonic acids, and *m*- and *p*-benzene-disulphonic acids with potash. The last mentioned compounds are employed for its preparation on the technical scale. It also results from the distillation of the extract of Brazil wood. White rhombic prisms or tables which quickly become brown in the air, dissolve easily in water, alcohol and ether, and reduce an aqueous solution of silver nitrate when warmed with it, and an alkaline solution even in the cold. With Fe_2Cl_6 resorcin gives a dark violet colouration. It acts therapeutically like carbolic acid, only more mildly.

It yields dyes with N_2O_3. When heated with phthalic anhydride it is converted into fluoresceïn (see eosin ; test for *m*-dioxy-benzenes), and it is therefore prepared on the large scale. Diazo-compounds transform it into azo-dyes, (cf. p. 403).

Its trinitro-derivative is **Styphnic acid**, $C_6H(OH)_2(NO_2)_3$, which is formed by the action of nitric acid upon many gum-resins.

Hydroquinone, $C_6H_4(OH)_2$ (1 : 4), (*Wöhler*, 1844).

Formation. By the oxidation of quinic acid, $C_7H_{12}O_6$, by means of PbO_2, by the saponification of arbutin, and from succino-succinic ether as given at p. 354, etc.

Preparation. By the oxidation of aniline with chromic acid

mixture, and also by the reduction of quinone with sulphur dioxide. Small monoclinic plates or hexagonal prisms, of about the same solubility as its isomers and capable of being sublimed. Ammonia colours it reddish-brown, while chromic acid, ferric chloride, and *other oxidizing agents convert it into quinone and eventually into quinhydrone* (p. 428). B. Pt. 285°. Being a strong reducing agent, it is used as a developer in photography (cf. also B. **25**, Ref. 432).

Acetate of lead yields a white precipitate with a solution of pyrocatechin, but none with resorcin, while hydroquinone is only precipitated in presence *of ammonia. From the observed heat of neutralization, resorcin and* hydroquinone behave towards soda as dibasic acids, and pyrocatechin as a weak monobasic acid.

(*b.*) **Dioxy-toluenes**, $C_6H_3(CH_3)(OH)_2$. Among the various isomerides which have been prepared (see B. **15**, 2995), there may be mentioned:

1. **Orcin**, *($CH_3 : OH : OH$ = 1 : 3 : 5), which is found in many lichens* (Rocella tinctoria, Lecanora, etc.). It results from orsellinic acid with separation of CO_2, *e.g.* upon fusing extract of aloes with potash, and it can also be prepared synthetically from toluene (B. **15**, 2992). Of especial interest is its synthesis from acetone-dicarboxylic ether (p. 265) and sodium (B. **19**, 1446). It crystallizes in colourless prisms of sweetish taste which tend to become red, and whose aqueous solution is coloured bluish-violet by Fe_2Cl_6. It does not yield a fluoresceïn with phthalic anhydride. By *the oxidation of its ammoniacal solution in the air*, **Orcein**, $C_{28}H_{24}N_2O_7$, the chief constituent of the commercial orchil dye, is formed, a compound which is also prepared directly from the lichens named above. Related to it is the well-known colouring matter litmus.

2. **Homo-pyrocatechin**, $C_6H_3(CH_3)(OH)_2$, ($CH_3 : OH : OH$ = 1 : 3 : 4) deserves mention on account of its mono-methyl ether **Creosol**, $C_6H_3CH_3(OH)(O.CH_3)$, occurring in beech-wood tar. Creosol is a liquid similar to guaiacol, boiling at 220°, and, as a derivative of pyrocatechin, *giving a green colouration with* Fe_2Cl_6.

3. Among the other isomers are **Cresorcin**, **Tolu-hydroquinone**, etc.

(*c.*) Homologous with the above are *e.g.* **Xylorcin** ($CH_3 : CH_3 : OH : OH$ = 1 : 3 : 4 : 6) and Beta-orcinol (*m*-dioxy-*p*-xylene), $C_6H_2(CH_3)_2(OH)_2$; **Mesorcin**, $C_6H(CH_3)_3(OH)_2$, ($CH_3 : CH_3 : CH_3 : OH : OH$ = 1 : 3 : 5 : 2 : 4) (see table, p. 412); **Thymo-hydroquinone**, $C_{10}H_{14}O_2$, which is present in Arnica montana, etc.

(*d.*) **Eugenol**, $C_{10}H_{12}O_2$, = $C_6H_3(OH)(OCH_3)(CH_2.CH{=}CH_2)$, the chief constituent of oil of cloves, is a derivative of an unsaturated diatomic phenol.

(*e.*) **Quinitol** (1,4-*Cyclo-hexane-diol*), *p-Dioxy-hexamethylene*, $C_6H_4.H_6.(OH)_2$, a diatomic phenol of reduced benzene, is obtained synthetically by the reduction of *p*-diketo-hexamethylene. It crystallizes in crusts and has a sweet taste with a bitter after-taste; M. Pt. 144°. It is the simplest representative of the Inosite-sugar group (p. 427). From quinitol a series of derivatives of reduced benzene can be prepared (*Baeyer*, B. **25**, 1037; **26**, 229).

C. Triatomic Phenols.

$C_6H_3(OH)_3$ { Pyrogallol = 1 : 2 : 3 = *v*; Phloroglucin = 1 : 3 : 5 = *s*; Oxy-hydroquinone = 1 : 2 : 4 = *a* } See table, p. 412.

1. **Pyrogallol**, *pyrogallic acid* (*Scheele*, 1786), is the most important of these three isomers. It is obtained, apart from synthetical reactions, by heating gallic acid, CO_2 being split off:
$$C_6H_2(OH)_3.CO_2H = C_6H_3(OH)_3 + CO_2.$$
It crystallizes in white plates, M. Pt. 132°, readily soluble in water and capable of subliming without decomposition. It is an energetic reducing agent, *e.g.* for silver salts, and its alkaline solution rapidly absorbs oxygen from the air, hence it is used in gas analysis, as a developer in photography, and so on. The aqueous solution is coloured bluish-black by a solution of ferrous sulphate containing ferric salt, and purple-red by iodine. It does not react with hydroxylamine (cf. phloroglucin).

Pyrogallol dimethyl ether, $C_6H_3(OH)(OCH_3)_2$ (*Hofmann*), is contained in beech-wood tar, as are likewise the dimethyl ethers of the compounds $C_6H_2(CH_3)(OH)_3$ and $C_6H_2(C_3H_7)(OH)_3$, homologous with pyrogallol.

2. **Phloroglucin** (*Hlasiwetz*, 1855) results from the fusion of various resins and of resorcin with potash or soda, by the action of alkali upon phloretin, and by fusing its tricarboxylic ether (whose synthetical formation is given on p. 354) with potash. Large prisms which weather in the air and sublime without decomposition; M. Pt. 218°. Gives with Fe_2Cl_6 a dark violet colouration.

Its reactions (analogous to those of succino-succinic ether) partly agree with the formula $C_6H_3(OH)_3$, *e.g.* it forms metallic compounds and a **Trimethyl ether**, $C_6H_3(O.CH_3)_3$, insoluble in alkali; but, on the other hand, it yields with hydroxylamine, like the ketones, a **Trioxime**, $C_6H_6(N.OH)_3$, and therefore appears readily to build up the atomic group

$$\underbrace{CH_2—CO—CH_2—CO—CH_2—CO}, = \textbf{Tri-keto-hexa-methylene},$$

which is termed the secondary or *pseudo*-form, in contradistinction to the first-named (the tertiary). (Cf. pp. 286 and 349; also B. **19**, 159, 2186; **23**, 1272. For the special constitution of the benzene ring in tertiary phloroglucin, see p. 349.)

The action of chlorine upon phloroglucin yields, among other products, **Hexachloro-triketo-hexamethylene**, $C_6Cl_6O_3$, which can be split up into dichloro-acetic acid and tetrachloro-acetone, and further into chlorinated acetyl-acetone, etc. (*Zincke* and *Kegel*, B. **22**, 1467; **23**, 230).

3. **Oxy-hydroquinone** results from the fusion of hydroquinone with potash (B. 16, 1231). Like pyrogallol it does not react with hydroxylamine.

D. Tetra-, penta- and hexatomic Phenols.

Tetr-oxy-benzene, $C_6H_2(OH)_4$ (1 : 2 : 4 : 5), can be prepared from dinitroresorcin (B. 21, 2374). It crystallizes in small gray plates with a silvery lustre; M. Pt. 215°–220°. Its chloro-derivative, **Dichloro-tetroxy-benzene,** $C_6Cl_2(OH)_4$, is readily oxidizable to chloranilic acid (see p. 429).

Hex-oxy-benzene, $C_6(OH)_6$, forms as potassium salt the so-called *Potassium carboxide*, $C_6O_6K_6$. It crystallizes in colourless readily oxidizable prisms, and can be converted into its quinone (tri-quinoyl), C_6O_6 (p. 430). It has also been prepared synthetically (B. 18, 499, 1833).

The following are perhaps to be regarded as polyatomic phenols of reduced benzene:—**Quercite,** $C_6H(H_6)(OH)_5$ (in Quercus), and **Inosite** or *Phaseo-mannite*, $C_6H_6(OH)_6$, a substance resembling sugar, which is found in the animal organism (the muscles of the heart) and in many plants (unripe beans, peas, and lentils). It forms large crystals which weather in the air, and exists in a dextro-, a lævo-, and an inactive modification.

Pinite, $C_7H_{14}O_6$, which occurs in Pinus Lambertiana, and which also resembles sugar, likewise belongs to this class, seeing that hydriodic acid reacts with it to produce methyl iodide and inosite.

E. Quinones.

Quinone, $C_6H_4O_2$ (1838). Quinone is produced when chromic acid is added to a solution of hydroquinone. It crystallizes in yellow needles or prisms of a characteristic pungent odour something like that of nut shells, sparingly soluble in water but readily in alcohol and ether, and capable of sublimation; M. Pt. 116°. Corresponding to it we have a large number of higher homologues, etc. These also are solids mostly of a yellow colour and volatile with steam; they result from the oxidation of the corresponding para-dioxy-compounds or of the higher atomic phenols, which contain two hydroxyls in the para-position.

The isomeric dioxy-benzenes do not show this formation of quinone.

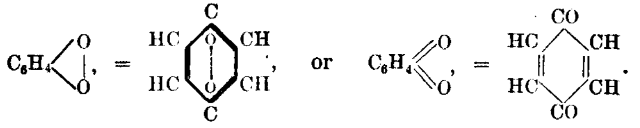
Quinone is also produced by the oxidation of many aniline and phenol derivatives belonging to the para-series, *e.g.* *p*-amido-phenol, sulphanilic acid and *p*-phenol-sulphonic acid; further, by the oxidation of aniline itself by means of chromic

acid, (see B. 19, 1467). It was first obtained by distilling quinic acid with manganese dioxide and sulphuric acid. Quinone readily volatilizes with steam, but at the same time much of it is decomposed. Exposure to light causes it to turn brown, and it colours the skin yellow-brown. It is easily converted into hydroquinone by reducing agents such as SO_2, HI, $SnCl_2$ and HCl etc., and can therefore act as an oxidizer.

In solution in chloroform it takes up two or four atoms of bromine to form a di- or tetra-bromide ($C_6H_4O_2.Br_4$). Under other conditions chlorine and bromine act upon it as substituents, while hydrochloric acid forms **Mono-chloro-hydroquinone**: $C_6H_4O_2 + HCl = C_6H_3Cl(OH)_2$.

It yields sparingly soluble crystalline compounds with primary amines and also (coloured) compounds with phenols. It is soluble in alkalies, the solution decomposing rapidly. With hydroquinone it forms an addition-compound termed **Quinhydrone**, $C_6H_4O_2 + C_6H_4(OH)_2$, crystallizing in green prisms with a metallic glance, which also results as an intermediate product in the oxidation of hydroquinone or in the reduction of quinone.

Constitution. Quinone is derived from benzene by the exchange of two atoms of hydrogen for two of oxygen which, from the close connection between quinone and hydroquinone, must be *in the p-position*. The *constitution of quinone may* be explained either by assuming that these two oxygen atoms are linked together as in peroxide of hydrogen, H—O—O—H, so that the benzene nucleus remains unchanged, or that the latter experiences a partial reduction, with the formation of a derivative of C_6H_8, a "diketo-dihydro-benzene":



According to the first of these two formulæ quinone would be a peroxide, according to the second, a ketone (quinone $= C_2H_2{<}^{CO}_{CO}{>}C_2H_2$). In favour of the latter view (which was brought forward by *Fittig*, and is now almost universally accepted) are (1) the fact that quinone can be converted into an oxime, $C_2H_2{<}^{C(N.OH)}_{CO}{>}C_2H_2$ (identical with nitroso-phenol, p. 419),

and into a dioxime, **Quinone dioxime**, $C_2H_2\!<\!\begin{matrix}C(N.OH)\\C(N.OH)\end{matrix}\!>\!C_2H_2$ (B. **20**, 613); (2) its power of forming addition-compounds with bromine; and (3) its relations to the analogously constituted anthraquinone. (Cf. B. **18**, 568; A. **223**, 170; J. pr. Ch. **42**, 161.)

The formation of succino-succinic ether, which was spoken of on p. 354, involves a synthesis of quinone. Succino-succinic acid is the dicarboxylic acid of a hypothetical dioxy-dihydro-benzene, $C_6H_4.H_2.(OH)_2$, and it can be transformed into the dicarboxylic acid of hydroquinone, $C_6H_4(OH)_2$, by the elimination of two atoms of hydrogen, and into bromanil (tetra-bromo-quinone) by bromine (cf. A. **211**, 306: B. **16**, 1412; **19**, 429, 1977; **23**, 1273).

Quinone tetra-hydride, $C_6H_4.H_4.(O_2)$, can be prepared by eliminating the carboxyls from succino-succinic ether, being thus obtained instead of the tautomeric hypothetical dioxy-dihydro-benzene (see above). It possesses the constitution of a *p-Diketo-hexamethylene* (*Cyclo-hexane-dione*),

$$\begin{matrix}CH_2-CO-CH_2\\|\qquad\qquad|\\CH_2-CO-CH_2\end{matrix}$$

. Colourless prisms; M. Pt. 78°. It yields quinitol upon reduction. Cf. B. **22**, 2168; **23**, 1272.

Quinone dioxime, $C_6H_4\!<\!\begin{matrix}N.OH\\N.OH\end{matrix}$, results from the action of hydroxylamine upon nitroso-phenol (B. **20**, 613; **21**, 428).

Chlorinated, etc., products are derived from hydroquinone as well as from quinone.

Chloranil, *tetrachloro-quinone*, $C_6Cl_4O_2$, which crystallizes in lustrous yellow plates, is obtained by chlorinating quinone and also by oxidizing many organic compounds, *e.g.* phenol, with HCl and $KClO_3$. It goes into tetra-chloro-hydroquinone, a colourless compound, upon reduction, and acts as an oxidizing agent, converting *e.g.* dimethyl-aniline into a methyl violet. A dilute solution of potash transforms it into **potassium chloranilate**, $C_6Cl_2O_2(OK)_2 + H_2O$ (dark red needles), corresponding to which there is also an analogous nitro-compound, **potassium nitranilate**, $C_6(NO_2)_2O_2(OK)_2$. The latter salt is distinguished by its sparing solubility, hence its formation may be made use of as a test for potassium compounds. For its constitution, see B. **19**, 2398.

By the action of chlorine upon chloranil and chloranilic acid, there result a series of complex chloro-products of the hexa- and penta-methylene series, and finally chlorinated fatty compounds. For a tabular summary, see *Hantzsch*, B. **22**, 2841; cf. also B. **25**, 827, 842.

As homologues of quinone may be mentioned **Tolu-quinone,** $C_6H_3(O_2)(CH_3)$, **Xylo-quinone,** $C_6H_2(O_2)(CH_3)_2$, **Thymo-quinone,** $C_6H_2(O_2)(CH_3)(C_3H_7)$, etc.

Several of these can be prepared synthetically by the condensation of 1 : 2 di-ketones, for instance di-acetyl yields xyloquinone under the influence of *alkali* (cf. B. **21**, 1411):

$$\begin{array}{l} CH_3-CO-CO-CHH_2 \\ +H_2CH-CO-CO-CH_3 \end{array} = \begin{array}{c} CH_3-C-CO-CH \\ \quad\ \| \qquad\quad \| \\ HC-CO-C-CH_3 \end{array} + 2H_2O.$$

Dioxy-quinone, $C_6H_2(O_2)(OH)_2$, which corresponds to tetroxy-benzene (p. 427), forms dark yellow needles (B. **21**, 2374). It is the mother substance of chlor- and nitranilic acids, mentioned above.

From hexoxy-benzene there can be prepared **Tetroxy-quinone,** $(C_6(O_2)(OH)_4$, **Dioxy-diquinoyl** or *rhodizonic acid*, $C_6(O_2)(O_2)(OH)_2$, and finally **Tri-quinoyl,** $C_6(O_2)(O_2)(O_2)+8H_2O$. In both the latter compounds the formation of quinone has taken place more than once (cf. B. **18**, 499, 1833; **23**, 3136, etc.).

F. Quinone-aniles and Anilido-quinones.

Aromatic bases, especially aniline, can so act on certain quinones that—with the aid of a simultaneous oxidation process—the group $(NHC_6H_5)'$ replaces hydrogen in the nucleus once or twice. There are thus formed "*Anilido-quinones*," which are mostly red or dark-coloured crystalline compounds. On the other hand, the quinonic oxygen may be replaced by the group $(NC_6H_5)''$, in which case "Quinone-aniles" result.

Both of these changes are represented (*e.g.*) in **Azo-phenine** or *Dianilido-quinone-dianile*, $C_6H_2(NHC_6H_5)_2'(NC_6H_5)_2''$. This results from aniline, more especially by heating it with azo-, amido-azo-, or nitroso-compounds in presence of hydrochloric acid. Small red plates. On further heating with aniline it yields induline dyes (*O. Fischer* and *E. Hepp*, A. **262**, 247).

G. Quinone Chlor-imides.

Related to the quinones are the **quinone chlor-imides,** which result from the oxidation of the *p*-amido-phenols or *p*-phenylene-diamines by means of chloride of lime.

Quinone chlor-imide, $C_6H_4(O)(NCl)$, *results from* HCl-*p-amido-phenol*, and **quinone dichlor-imide,** $C_6H_4(NCl)_2$, from HCl-*p*-phenylene-diamine. The first named crystallizes in golden yellow crystals which are volatile with steam; reduction converts it into amido-phenol, and boiling with

water into quinone, the dichloro-compound behaving in an analogous manner. For these compounds the following constitutional formulæ are assumed:

$$C_6H_4\begin{matrix}\diagup O \\ \diagdown N.Cl\end{matrix} \text{ or } C_6H_4\begin{matrix}\diagup O \\ \diagdown \dot{N}.Cl\end{matrix} \quad\text{and}\quad C_6H_4\begin{matrix}\diagup N.Cl \\ \diagdown N.Cl\end{matrix} \text{ or } C_6H_4\begin{matrix}\diagup NCl \\ \diagdown \dot{N}Cl\end{matrix}$$

Quinone chlor-imide. Quinone dichlor-imide.

These formulæ are based upon the fact that derivatives of diphenylamine result from their action upon phenols or amines. (See Indo-phenols, p. 389.)

XXIV. AROMATIC ALCOHOLS, ALDEHYDES AND KETONES.

A. Aromatic Alcohols.

While the phenols remind us of the tertiary alcohols of the fatty series in their properties, although they differ from these in many points, we are acquainted at the same time with real aromatic alcohols, *i.e.* compounds which possess the alcoholic character in its entirety. The most important of these is (primary) benzyl alcohol, $C_7H_7.OH$, which is isomeric with the cresols, this isomerism being explained by the different position of the hydroxyl in the molecule; thus, while the cresols, like all phenols, contain the hydroxyl linked to the benzene nucleus, it is present in the side chain in benzyl alcohol:

$C_6H_4(CH_3).OH$, Cresols; $C_6H_5—CH_2.OH$, Benzyl alcohol.

This follows from the formation of benzyl alcohol from benzyl chloride, $C_6H_5—CH_2Cl$ (and *vice versa*), and also from the fact that it can be oxidized to an aldehyde and an acid containing the same number of carbon atoms in the molecule as itself, these being likewise mono-derivatives of benzene:

$C_6H_5—CH_2.OH$	$C_6H_5—CHO$	$C_6H_5—CO.OH$
Benzyl alcohol.*	Benzaldehyde.†	Benzoic acid.‡

Benzyl alcohol may also be looked upon as methyl alcohol in which one atom of hydrogen is replaced by the group C_6H_5:

$CH_2\begin{matrix}\diagup H \\ \diagdown OH\end{matrix}$	$CH_2\begin{matrix}\diagup C_6H_5 \\ \diagdown OH\end{matrix}$
Methyl alcohol, = carbinol.	Benzyl alcohol, = phenyl carbinol.

It is therefore the simplest existing aromatic alcohol.

* Benzene-methylol. † Benzene-methylal. ‡ Benzene-carboxylic acid.

Among its homologues the following primary and secondary alcohols may be mentioned (tertiary being also known):

$C_8H_9.OH$	$C_6H_4(CH_3)—CH_2.OH$ Tolyl alcohols.	$C_6H_5—CH_2—CH_2.OH$ and $C_6H_5—CH(OH)—CH_3$ Phenyl-ethyl alcohols.
$C_9H_{11}.OH$	$C_6H_4(C_3H_7)-CH_2.OH$ Cumic alcohol (*p*).	$C_6H_5-CH_2-CH_2-CH_2.OH$ Phenyl-propyl alcohol, etc.

Di- and triatomic alcohols likewise exist; these must contain not less than 8 and 9 atoms of carbon in the molecule respectively (see p. 203, etc.), *e.g.*:

$C_8H_{10}O_2$	$C_6H_4(CH_2.OH)_2$: { *p* = Tolylene glycol. *o* = Phthalyl alcohol.
$C_9H_{12}O_3$	$C_6H_5—CH(OH)—CH(OH)—CH_2.OH$ Phenyl-glycerine (stycerine), etc.

All these compounds are, as alcohols, perfectly analogous to the alcohols of the fatty series, so far as regards the formation of alcoholates, ethers, compound ethers, mercaptans, amines, phosphines, etc. They are however benzene derivatives at the same time, and consequently yield chloro-, bromo-, nitro-, amido-, etc., substitution products. By the entrance of the phenyl group into unsaturated fatty alcohols, there result *unsaturated* aromatic alcohols which resemble the unsaturated compounds of the fatty series to the closest extent in their chemical behaviour, but are at the same time benzene derivatives.

These remarks also apply in full degree, *mutatis mutandis*, to the aromatic aldehydes and ketones (see below).

Benzyl alcohol, $C_6H_5—CH_2.OH$, is a colourless liquid of faint aromatic odour, sparingly soluble in water; B. Pt. 206°. It occurs naturally in Peru and Tolu balsams as benzoic and cinnamic ethers, and is formed from benzyl chloride just as alcohol is from ethyl chloride.

Preparation. By the reduction of its aldehyde or, better, by

the action of aqueous potash upon the latter, whereby the one half of it is oxidized and the other half reduced, (B. 14, 2394):

$$2C_6H_5—CHO + KOH = C_6H_5—CH_2.OH + C_6H_5—COOK.$$

Benzyl alcohol also results from the reduction of benzamide.

Benzyl hydrosulphide, $C_6H_5—CH_2.SH$, the corresponding thio-alcohol, is a liquid of most unpleasant odour and of typical mercaptanic character. The amine, **Benzylamine**, $C_6H_5—CH_2.NH_2$, has been already referred to on p. 393; homologous amines are also known.

Benzyl hydroxylamines are also known, *e.g.* $C_6H_5—CH_2—NH(OH)$, this latter existing in different isomeric modifications.

Phenyl-methyl carbinol, $C_6H_5—CH(OH)—CH_3$, B. Pt. 203°, can be prepared by reducing acetophenone, $C_6H_5—CO—CH_3$ (p. 435), into which it is reconverted by gentle oxidation.

The simplest of the unsaturated alcohols is **Cinnamic alcohol** or *styrone*, $C_9H_{10}O$, = $C_6H_5—CH=CH—CH_2(OH)$, which occurs as cinnamic ether ("styracin") in storax. It crystallizes in glancing needles of hyacinth-like odour, and goes into cinnamic acid when oxidized gently, and into benzoic when the oxidation is more vigorous. As an alcohol it forms ethers, etc.

B. Aromatic Aldehydes.

Benzoic aldehyde,* *benzaldehyde*, or *oil of bitter almonds*, $C_6H_5—CHO$. Discovered in 1803; investigated by *Liebig* and *Wöhler*, (A. 22, 1). Colourless, strongly refracting liquid of agreeable bitter almond oil odour. B. Pt. 179°; Sp. Gr. at 15°, 1·05. Readily soluble in alcohol and ether, but only sparingly in water (1 in 30).

Modes of formation. These are for the most part analogous to those of the fatty aldehydes. It results:

(*a*) From the oxidation of the corresponding alcohol.

(*b*) From the reduction of the corresponding acid (distillation of a mixture of benzoate and formate of calcium).

(*c*) By heating the corresponding dichloride, benzal chloride, also called benzylene dichloride, $C_6H_5—CHCl_2$ (from toluene), with water or sulphuric acid, or, as is done on the technical scale, with water and hydrate of lime; also by heating benzyl chloride, $C_6H_5—CH_2Cl$, with water and lead nitrate.

(*d*) Together with dextrose and hydrocyanic acid by decomposing amygdalin, $C_{20}H_{27}NO_{11}$, a compound which occurs in

* Benzene-methylal.

bitter almonds and crystallizes in white plates (p. 273), either by means of sulphuric acid or by emulsin (an enzyme likewise present in bitter almonds, cf. p. 322):

$$C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5—CHO + 2C_6H_{12}O_6 + CNH.$$

(*c*) By the action of chromyl chloride, CrO_2Cl_2, upon toluene. This is the *Etard* reaction, an important one for the synthesis of aldehydes and also of certain ketones from hydrocarbons (B. **17**, 1462, 1700; cf. also p. 360).

Behaviour. 1. Its behaviour is that of an aldehyde in every respect. Thus it is: (*a*) easily oxidizable to the acid, and it reduces an ammoniacal silver solution with the production of a mirror; (*b*) reducible to the alcohol; (*c*) capable of forming an addition-compound with $NaHSO_3$ (but not one with NH_3, giving in the latter case hydro-benzamide, $(C_6H_5CH)_3N_2$, with elimination of H_2O); (*d*) capable of combining with HCN (see mandelic acid); (*e*) condensible with other aldehydes and also with acids and ketones of the fatty series, *e.g.* to cinnamic acid (B. **14**, 2460; **15**, 2856); also with dimethyl-aniline, phenols, etc., to triphenyl-methane derivatives; (*f*) capable of combining with hydroxylamine and phenyl-hydrazine to benzaldoxime, $C_6H_5—CH{=}N.OH$, and benzaldehyde-phenyl-hydrazone, $C_6H_5—CH{=}N_2H—C_6H_5$, respectively (a delicate reaction, cf. B. **17**, 574).

2. It also behaves in every respect like a benzene derivative, in that it is capable of being substituted by halogens (indirectly), and of being nitrated, amidated, sulphurated, etc. (directly).

As in the case of toluene, chlorine enters the side chain here at the boiling temperature, with formation of benzoyl chloride, $C_6H_5—COCl$.

Among its derivatives, the following deserve mention:—

α-Benzaldoxime, *Benz-anti-aldoxime,* $C_6H_5—CH{=}N.OH$, a liquid which results from benzoic aldehyde and hydroxylamine, and which undergoes decomposition on boiling. It can be transformed into the isomeric solid **β-Benzaldoxime,** *Benz-syn-aldoxime,* which, in contradistinction to the other, passes readily into benzo-nitrile with acetic anhydride. Both oximes are structurally identical, but stereo-isomeric (Nitrogen-isomerism). Cf. p. 158; also *Hantzsch,* B. **24**, 15, 3481.

Benzaldehyde phenyl-hydrazone, $C_6H_5—CH{=}(N_2HC_6H_5)$. Colourless crystals, M. Pt. 152°.

Hydro-benzamide, $C_{21}H_{18}N_2 = N_2(=CH.C_6H_5)_3$. From benzoic aldehyde and ammonia. Rhombic crystals, M. Pt. 110°.

A **Dihydro-benzaldehyde**, $C_6H_5(H_2)$—CHO, has also been prepared by splitting up *anhydro-ecgonine* (which see; also B. **23**, 2870). Gentle oxidation converts it into dihydro-benzoic acid (B. **26**, 454).

Nitro-benzaldehydes, $C_6H_4(NO_2)CHO$. The *m*-compound is formed in largest proportion upon nitrating, but at the same time the *o*-compound to the extent of 20 p. c. The latter can be best prepared by oxidizing *o*-nitro-cinnamic acid by $KMnO_4$ in presence of benzene (B. **17**, 121). Long colourless needles, M. Pt. 46°. It is particularly interesting on account of its convertibility into indigo by means of acetone and caustic soda (B. **15**, 2856), and its reducibility to *o*-**Amido-benzaldehyde**, $C_6H_4(NH_2)CHO$, a compound crystallizing in silvery glancing plates, M. Pt. 40°, which is of value for various synthetical reactions. (See Quinoline; also B. **16**, 1833.) *m*-**Amido-benzaldehyde**, which is prepared from *m*-nitro-benzaldehyde, and especially by the reduction of its bisulphite compound, is used in the production of triphenyl-methane dyes.

Among its homologous aldehydes we have the three **Toluic aldehydes**, $C_6H_4(CH_3)$—CHO, together with the isomeric **Phenyl-acetic aldehyde**, C_6H_5—CH_2—CHO; further, **Cumic aldehyde**, *cuminol* or *isopropyl-benzaldehyde*, $C_6H_4(C_3H_7)$—CHO, which is contained in Roman oil of cumin.

Phenyl-tetrose, $C_6H_5(CH.OH)_3CHO$, at the same time an aldehyde and a polyatomic alcohol, represents an aromatic sugar; it can be synthetized (B. **25**, 2559).

As an example of a diatomic aldehyde, **Terephthalic aldehyde**, $C_6H_4(CHO)_2$ (1 : 4), may be taken.

Cinnamic aldehyde, C_6H_5—CH=CH—CHO, is the chief constituent of oil of cinnamon (Persea cinnamomum), from which it may be isolated by means of its $NaHSO_3$-compound. It is an oil of aromatic odour which boils at 246°, and readily distils along with steam.

C. Aromatic Ketones.

Acetophenone, C_6H_5—CO—CH_3, is the simplest representative of the (mixed) aromatic ketones. It crystallizes in colourless plates, readily soluble in water, M. Pt. 20°, B. Pt. 200°, and is obtained by the normal modes of preparation for ketones (*e.g.* by distilling a mixture of acetate and benzoate of calcium), as also by the conjoint action of acetyl chloride and aluminium chloride upon benzene. It unites in itself the properties of a ketone of the fatty series and of a benzene derivative. It yields benzoic acid and carbon dioxide upon oxidation (or,

under other conditions, benzoyl-formic acid), is substituted in the side chain by halogens when heated (*e.g.* to "**Phenacyl bromide,**" $C_6H_5—CO—CH_2Br$), and is nitrated by HNO_3, etc. It is used as a soporific under the name of "*Hypnone.*"

Its homologues resemble it in every respect, but are liquid at the ordinary temperature. Acetophenone and some of its homologues can be prepared from hydrocarbons with long side chains, by the *Étard* reaction (see p. 434; B. **23**, 1070, **24**, 1356). The ketone proper of benzoic acid, Benzophenone, $C_6H_5—CO—C_6H_5$, is described on p. 482. Aromatic poly-ketones (cf. p. 238) have also been prepared, *e.g.* **Benzoyl-acetone,** $C_6H_5—CO—CH_2—CO—CH_3$, and **Acetophenone-acetone,** $C_6H_5—CO—CH_2—CH_2—CO—CH_3$. The latter like acetonyl-acetone, is readily converted into furfurane, pyrrol and thiophene derivatives (see p. 328), *e.g.* into phenyl-methyl-pyrrol, $C_4H_2(C_6H_5)(CH_3).NH$.

D. Oxy-alcohols and -aldehydes; Ketone-alcohols.

Summary.

$C_6H_4<^{OH}_{CH_2.OH}$ *o*-: Saligenin. *m*-, *p*-: Oxy-benzyl alcohols.	$C_6H_4<^{OH}_{CHO}$ *o*-: Salicylic aldehyde. *m*-, *p*-: Oxy-benzaldehydes.
$C_6H_4<^{OCH_3}_{CH_2.OH}$ *p*: = Anisyl alcohol.	$C_6H_4<^{OCH_3}_{CHO}$ Anisaldehyde.
	C_6H_3—OH (4), —OH (3), —CHO (1) = Protocatechuic aldehyde.
C_6H_3—OH (4), —OCH_3 (3), —$CH_2.OH$ (1) = Vanillic alcohol.	C_6H_3—OH (4), —OCH_3 (3), —CHO (1) = Vanillin.

etc., etc.

A large number of compounds are known which unite in themselves the properties of a phenol and of an alcohol or aldehyde. They are derived from the simple alcohols, etc. by the entrance of hydroxyl into the benzene nucleus.

Several of these compounds occur in nature, *e.g.* saligenin is a constituent of salicin (see the glucosides), while salicylic aldehyde is found in spiræa varieties and vanillin in the vanilla

capsules. Anisaldehyde results from the oxidation of anisol (methyl phenate).

Oxy-aldehydes are formed synthetically by the action of chloroform upon an alkaline solution of phenol, of dioxy-benzene, of monomethyl-dioxy-benzene, etc.; *e.g.* 1 : 2- and 1 : 4-oxy-benzaldehydes from phenol, *protocatechuic aldehyde from pyrocatechin, and vanillin from guaiacol.* (See p. 443, 4*f.*)

Vanillin, *methyl-protocatechuic aldehyde*, $C_8H_8O_3$, which crystallizes in beautiful needles, is prepared on the large scale from **Coniferin**, $C_{16}H_{22}O_8 + 2H_2O$, a compound occurring in the sap of the cambium in the coniferæ. This is broken up by acids into glucose and **Coniferyl alcohol**, $C_6H_3(OH)(OCH_3)(C_3H_4.OH)$, which latter goes into vanillin upon oxidation, (*Tiemann* and *Haarmann*); the CH_3-group is split off upon heating with hydrochloric acid to 200°, with the formation of protocatechuic aldehyde. Vanillin is also found *e.g.* in asparagus, raw beet sugar and asafœtida, and it likewise results from the oxidation of olive wood, etc.

Vanillin can also be obtained synthetically from *m*-chloro-*p*-nitro-benzaldehyde (from *m*-chloro-*p*-nitro-toluene), and also from eugenol.

Benzoyl carbinol, *oxy-acetophenone*, $C_6H_5—CO—CH_2.OH$, is a ketonic alcohol which can be prepared from the bromide, $C_6H_5—CO—CH_2Br$, and which crystallizes in glancing plates. It resembles acetone-alcohol, although it is more stable than the latter, and has like it strongly reducing properties, reducing alkaline silver and copper solutions even in the cold. It yields an osazone with phenyl-hydrazine.

Phenyl-glyoxal, $C_6H_5—CO—CHO$, is the corresponding ketonic aldehyde. Cf. the analogous pyro-racemic aldehyde, and also B. **22**, 2556.

XXV. Aromatic Acids.

The aromatic acids are analogous to the fatty acids in most respects. As acids they are capable of forming exactly the same kinds of derivatives as the latter, *i.e.* salts, compound ethers, chlorides, anhydrides, amides, etc., *e.g.*:

$C_6H_5.CO_2H$, Benzoic acid.

$C_6H_5.CO_2(C_2H_5)$, Ethyl benzoate; $(C_6H_5.CO)_2O$, Benzoic anhydride;

$C_6H_5.CO.Cl$, Benzoyl chloride; $C_6H_5.CO.NH_2$, Benzamide; etc.

But they are at the same time benzene derivatives and, as

such, can undergo most of the transformations of which benzene itself is capable. Thus chlorine, bromine and iodine substitution products and nitro-, amido- and sulphonic acids, etc. can be prepared from them, the amido-acids can be diazotized, and, upon the entrance of oxygen into the benzene nucleus, there result phenolic acids (*i.e.* compounds which possess the characters of phenols and of acids), quinone acids, (*i.e.* compounds at once a quinone and an acid), etc.

Alcohol-acids, ketone-acids, etc., are likewise capable of existence in the aromatic as well as in the fatty series.

We have, for instance, the following derivatives:

$C_6H_4Cl.CO_2H$, chloro-benzoic acids;
$C_6H_4(NO_2).CO_2H$, nitro-benzoic acids;
$C_6H_4(NH_2).CO_2H$, amido-benzoic acids;
$C_6H_4(SO_3H).CO_2H$, sulpho-benzoic acids;
$C_6H_4(OH).CO_2H$, oxy-benzoic acids;
$C_6H_5.CH(OH).CO_2H$, mandelic acid, etc.

Their modes of formation are likewise partly analogous to those of the fatty acids, (cf. p. 440 *et seq.*).

The homologous acids however do not here show the gradual changes in physical properties which the homologous fatty acids do.

Constitution. Corresponding to the aromatic acids there are again nitriles, *e.g.* to benzoic acid benzo-nitrile, $C_6H_5.CN$, which may also be regarded as cyanogen derivatives of the hydrocarbons (in the above case, cyano-benzene), and which are converted into the acids upon saponification. From this it follows that their constitution must correspond exactly with that of the fatty acids; like the latter they are characterized by the presence of carboxyl, CO.OH, in the molecule. There are monobasic, di-, tri- and up to hexabasic aromatic acids, according to the number of hydrogen atoms in the molecule which are readily replaceable by metal, *i.e.* according to the number of carboxyl-groups:

$C_6H_4(CO_2H)_2$	$C_6H_3(CO_2H)_3$	$C_6(CO_2H)_6$
Phthalic acids.	Benzene-tri-carboxylic acids.	Mellitic acid.

Unsaturated aromatic acids also exist in large number. They chiefly differ from the saturated acids in that, as un-

saturated compounds, they readily form addition-compounds with H_2, Cl_2, HCl, etc., going thereby into the saturated acids or their substitution products. In most of these additions the benzene nucleus remains unaltered (cf. p. 344, 3). Their constitution is therefore entirely analogous to that of the acids of the acrylic or propiolic series; they contain a side chain with a double or triple carbon bond:

$$C_6H_5—CH=CH—CO_2H \qquad C_6H_5—C\equiv C—CO_2H$$

Cinnamic acid. Phenyl-propiolic acid.

For the special constitution of the benzene ring in the aromatic acids, see p. 349.

Besides the aromatic acids proper, which have just been spoken of, other acids have recently become known, *which are derivatives either of a completely reduced or a partially reduced benzene*. The acids of the former series, *e.g.* the hexahydro-benzoic acids, behave in exactly the same manner as the saturated fatty acids; while those of the latter, *e.g.* the di- and tetrahydro-benzoic acids, resemble the unsaturated fatty acids. Cf. p. 349.

The aromatic oxy-acids, *e.g.* the oxy-benzoic acids, which possess at the same time phenolic and acid characters, manifestly contain phenol-hydroxyl (*i.e.* hydroxyl which is linked directly to the benzene nucleus) in addition to the carboxyl group or groups; they are capable of yielding salts either as acids or as phenols, but otherwise they correspond in many points with the alcohol-acids of the fatty series.

The true aromatic alcohol-acids, such as mandelic acid (phenyl-glycollic acid), which correspond completely with the latter, manifestly contain their alcoholic hydroxyl not in the benzene nucleus, but in the side chain, as is also the case with the aromatic alcohols.

Nomenclature. The most rational nomenclature* is the designation of the aromatic acids as carboxylic acids of the original hydrocarbons in question, *e.g.* phthalic acid is benzene-dicarboxylic acid. Many names, such as xylic acid, are taken from those of the hydrocarbons into which the carboxyl has entered, while others, such as mesitylenic acid, indicate the hydrocarbons from whose oxidation the acids result. An important principle as regards nomenclature depends upon the fact that aromatic acids can be derived from almost every fatty acid of any consequence by the exchange of H for C_6H_5, *e.g.*:

CH_3-CO_2H, acetic acid; C_6H_5-CH_2-CO_2H, phenyl-acetic acid.

There thus exist phenylated acids analogous to the acids of the acetic, glycollic, succinic, malic and tartaric series, etc. Atropic acid, $C_6H_5—C\lessgtr^{CH_2}_{CO_2H}$, for example, may be designated α-phenyl-acrylic acid, and so on.

* For "official names" see p. 28.

Properties. Most of the aromatic acids are solid crystalline substances, generally only sparingly soluble in water and therefore precipitable by acids from solutions of their salts, but often readily soluble in alcohol and ether. The simpler among them can be distilled or sublimed without decomposition, while the more complicated, especially phenolic and poly-carboxylic acids, give up carbon dioxide when heated; *e.g.* salicylic acid, $C_6H_4(OH).CO_2H$, breaks up thus into phenol and CO_2. Such a separation of carbonic anhydride is effected in the case of those acids which are volatile without decomposition by heating *e.g.* with soda-lime; in polybasic acids the carboxyls may be split up in succession:

$$C_6H_4(CO_2H)_2 = C_6H_5(CO_2H) + CO_2 = C_6H_6 + 2CO_2.$$

Occurrence. A large number of the aromatic acids are found in nature, *e.g.* in many resins and balsams, and also in the animal organism in the form of nitrogenous derivatives such as hippuric acid.

Modes of formation.

A. Of the saturated acids.

1. By the oxidation of the corresponding primary alcohols or aldehydes; *e.g.* benzoic acid from benzyl alcohol.

2. By the oxidation of the benzene homologues and of all the compounds which are derived from these by substitutions in the side chain; also of all the derivatives of those compounds which contain halogen, nitro-, sulpho-, etc. groups, hydroxyl or carboxyl in place of benzene hydrogen:

$C_6H_5(CH_3)$	yields	$C_6H_5(CO_2H)$
$C_6H_4(CH_3)_2$ $C_6H_4(CH_3)(C_3H_7)$	,,	$C_6H_4(CO_2H)_2$
$C_6H_3(CH_3)_2(C_2H_5)$	,,	$C_6H_3(CO_2H)_3$
$C_6H_5—CH_2(NH_2)$	,,	$C_6H_5—CO_2H$
$C_6H_4Cl(CH_3)$	,,	$C_6H_4Cl(CO_2H)$
$C_6H_4(NO_2)(C_2H_5)$	,,	$C_6H_4(NO_2)(CO_2H)$
$C_6H_3(OH)_2(CH_3)$	,,	$C_6H_3(OH)_2(CO_2H)$
$C_6H_4(CH_3)(CO_2H)$	,,	$C_6H_4(CO_2H)_2$
$C_6H_5—CH=CH—CO_2H$	,,	$C_6H_5—CO_2H.$

Should there be several side chains in the molecule, they are usually all converted directly into carboxyl by chromic acid, whereas by

using dilute nitric acid, this transformation can be effected step by step, *e.g.* :

$C_6H_4(CH_3)_2$ yield first $C_6H_4(CH_3)(CO_2H)$ and then $C_6H_4(CO_2H)_2$
The xylenes Toluic acids Phthalic acids.

Nevertheless the three classes of isomeric benzene derivatives with two side chains comport themselves differently. The para-compounds are the most readily oxidized to acids by chromic acid mixture and then the meta-, whereas the ortho-compounds are either completely destroyed by it (p. 359) or not attacked at all. The last-named may however be oxidized in the normal manner by nitric acid or permanganate of potash. The entrance of a negative group (and also of hydroxyl) renders more difficult the oxidation of an alkyl-group having the *o*-position with regard to it (*cf.* p. 422).

3. By the saponification of the corresponding nitriles (p. 438).

$$C_6H_5.CN + 2H_2O = C_6H_5.CO_2H + NH_3.$$

These **Nitriles**, which can be prepared from the ammonium salts of the acids in the same manner as those of the fatty series, result from the following syntheses :

(*a*) By distilling the potash salts of the sulphonic acids with potassium cyanide or ferrocyanide (*Merz*), just as the nitriles of the fatty acids are formed from the alkyl sulphates (p. 117):

$$C_6H_5.SO_3K + KCN = C_6H_5.CN + SO_3K_2.$$

Nitriles cannot as a rule be prepared from chloro-benzenes, etc. and KCN, (cf. p. 367); the halogen is more readily replaced by cyanogen if sulpho-groups are likewise present. Or nitro-groups (in presence of halogens) can also be replaced, as in the case of the bromo-nitro-benzenes, (B. 8, 1418).

Benzyl chloride, $C_6H_5—CH_2Cl$, and all the haloid hydrocarbons which are substituted in the side chain, on the other hand, show the normal ready exchangeability of halogen for cyanogen :

$$C_6H_5—CH_2Cl + KCN = KCl + C_6H_5—CH_2.CN$$
Benzyl cyanide.

(*b*) By heating the mustard oils with copper or zinc dust (*Weith*) :

$$C_6H_5.NCS + 2Cu = C_6H_5CN + Cu_2S.$$

(*c*) By the molecular transformation of the isomeric iso-nitriles at a

somewhat high temperature: ($C_6H_5.NC = C_6H_5.CN$).

(*d*) By diazotizing the primary amines, and replacing the diazo-group by cyanogen, according to the *Sandmeyer* reaction (p. 396); or by first converting them into iso-thiocyanates or iso-nitriles, and treating these as given in (*b*) or (*c*).

(*e*) By eliminating the elements of water from the oximes of the aldehydes by means of acetyl chloride:

$$\text{Benzaldoxime, } C_6H_5.CH{=}N.OH = C_6H_5.CN + H_2O.$$

4. Syntheses effected by the action of carbonic acid or its derivatives:

(*a*) Benzoic acid, etc. is produced by the action of carbon dioxide upon mono-bromo-benzene, etc. in presence of sodium, (*Kekulé*):

$$C_6H_5Br + CO_2 + 2Na = C_6H_5.CO_2Na + NaBr.$$

(*b*) By the action of phosgene, $COCl_2$, or also of CO_2, upon benzene and its homologues in presence of Al_2Cl_6 (*Friedel* and *Crafts*):

$$C_6H_6 + COCl_2 = C_6H_5.COCl + HCl.$$

Acid chlorides are first formed here, which are then to be decomposed by water. By the further action of these chlorides upon benzene in presence of Al_2Cl_6, ketones result (see benzophenone.)

$COCl_2$ acts with particular ease upon tertiary amines:

$$C_6H_5.N(CH_3)_2 + COCl_2 = C_6H_4[N(CH_3)_2].COCl + HCl.$$

(*c*) By the action of carbamic chloride, $Cl{-}CO.NH_2$, upon benzene (or phenol) in presence of Al_2Cl_6, there result in an analogous manner the amides of the aromatic acids, which are readily saponified (*Gatterman*, A. **244**, 29):

$$C_6H_6 + Cl{-}CO.NH_2 = C_6H_5{-}CO.NH_2 + HCl.$$

(*d*) By the action of sodium upon a mixture of brominated benzenes and chloro-carbonic ether (*Wurtz*); in this case the compound ethers are first formed, but these are easy to saponify:

$$C_6H_5Br + Cl.CO_2(C_2H_5) + 2Na$$
$$= C_6H_5.CO_2(C_2H_5) + NaBr + NaCl.$$

(*e*) The phenolic acids are produced by passing carbon dioxide over heated sodium phenate, (*Kolbe*; see p. 455):

$$C_6H_5.ONa + CO_2 = C_6H_4(OH).CO_2Na.$$

In the case of the phenols of higher atomicity, *e.g.* resorcin, it often suffices merely to heat with a solution of ammonium carbonate or potassium bicarbonate, (B. 13, 930). Chlorocarbonic ether acts in a similar way.

(*f*) *p*-Oxy-acids are formed by the action of carbon tetrachloride upon phenols in alkaline solution, (B. 10, 2185):

$$C_6H_5ONa + CCl_4 = C_6H_4(OH).CCl_3 + NaCl.$$
$$C_6H_4(OH).CCl_3 + 4NaOH = C_6H_4(OH).CO_2Na + 3NaCl + 2H_2O.$$

When chloroform is employed, the aldehydes of these (*o*- and *p*-) oxy-acids result in an analogous manner:

$$C_6H_5.OH + CHCl_3 + 3NaOH = C_6H_4.(OH)CHO + 3NaCl + 2H_2O.$$

Methylene chloride, CH_2Cl_2, also shows a similar behaviour, with the formation of aromatic oxy-alcohols.

(*g*) By heating the sulphonates with sodium formate (*V. Meyer*):

$$C_6H_5.SO_3K + HCO_2K = C_6H_5.CO_2K + HSO_3K.$$

5. Aceto-acetic ether and malonic ether syntheses, etc.

(*a*) For the formation of phloroglucin-tricarboxylic ether from sodio-malonic ether, see p. 354.

Sodio-aceto-acetic ether yields a complicated benzene derivative in an analogous manner (B. 18, 3460).

(*b*) For the production of hydroquinone-dicarboxylic ether, etc. from ethyl succinate or from brom-aceto-acetic ether, see p. 354.

(*c*) For the action of aceto-acetic ether upon phenols, see p. 444.

(*d*) Aceto-acetic ether acts upon the haloid derivatives which are substituted in the side chain, *e.g.* benzyl chloride, exactly as in the fatty series, with the formation of the more complicated ketonic acids, which again are capable of undergoing either the "acid decomposition" or the "ketone decomposition" (p. 244), *e.g.*:

$$C_6H_5—CH_2Cl + CH_3—CO—CHNa—CO_2R = \underbrace{CH_3—CO—CH(C_7H_7)—CO_2R}_{\text{Benzyl-aceto-acetic ether.}} + NaCl.$$

$$CH_3—CO—CH(C_7H_7)—CO_2R + H_2O = \underbrace{C_6H_5—CH_2—CH_2—CO_2R}_{\text{Phenyl-propionic ether.}} + CH_3.CO_2H.$$

6. Alcohol-acids and ketone-acids are formed by exactly the same methods as in the fatty series (p. 222), *e.g.* mandelic acid by the combination of hydrocyanic acid with benzaldehyde, and saponification of the resulting nitrile, (B. 14, 239, 1965):

$$C_6H_5—CHO + HCN = C_6H_5—CH(OH)—CN;$$

or, from α-chlorophenyl-acetic acid, (B. 14, 239):

$$C_6H_5—CHCl—CO_2H + KOH = C_6H_5—CH(OH)—CO_2H + KCl.$$

7. Hydro-*p*-cumaric acid, hydrocinnamic acid, *p*-oxyphenyl-acetic acid, etc. are produced by the decay of albumen, (B. 16, 2313).

B. Of the unsaturated acids.

1. From the mono-haloid substitution products of the saturated acids in the normal manner (p. 178); similarly from the corresponding nitriles, primary alcohols, etc., as in the case of the saturated compounds.

2. According to the so-called *Perkin* reaction, by the action of aromatic aldehydes upon fatty acids. Thus, when benzaldehyde is heated with acetic anhydride and sodium acetate, cinnamic acid is formed:

$$C_6H_5.CHO + CH_3.CO_2Na = C_6H_5—CH{=}CH—CO_2Na + H_2O.$$

The acetic anhydride only acts as a dehydrating agent in this instance, the reaction taking place between the sodium acetate and the aldehyde (cf. A. 216, 101).

Oxy-acids are formed as intermediate products here by a reaction similar to "aldol condensation" (p. 145); in the above case, for instance, β-phenyl-hydracrylic acid, $C_6H_5—CH(OH)—CH_2—CO_2H$.

This reaction also takes place with the oxy-aldehydes, with the homologues of acetic acid, and also with dibasic acids, *e.g.* malonic.

Cinnamic acid is similarly produced by the action of sodium upon a mixture of benzoic aldehyde and ethyl acetate (B. 23, 976).

3. Cinnamic acid results in an analogous manner by the action of benzal chloride upon sodium acetate (*Caro*):

$$C_6H_5—CHCl_2 + CH_3—CO_2H = C_6H_5—CH{=}CH—CO_2H + 2HCl.$$

4. By the action of aceto-acetic ether upon the phenols in presence of concentrated H_2SO_4, there are formed unsaturated phenolic acids or their anhydrides (B. 16, 2119; 17, 2191), *e.g.*:

$$C_6H_5(OH) + \underbrace{\begin{matrix}(OH).C(CH_3){=}CH \\ HO—\dot{C}O\end{matrix}}_{\text{(Pseudo-form.)}} = \underbrace{C_6H_4\begin{matrix}\diagup C(CH_3){=}CH \\ \diagdown O \quad —\dot{C}O\end{matrix}}_{\text{Methyl-cumarin.}} + 2H_2O.$$

4a. Malic acid acts upon phenols in presence of H_2SO_4 in an analogous manner, reacting here probably as the half-aldehyde of malonic acid, $CHO \cdot CH_2 \cdot CO_2H$ (= malic acid, $C_2H_3(OH)(CO_2H)_2$, $- CO_2H_2$ [see p. 240]), (*v. Pechmann*, B. **17**, 929):

$$C_6H_5.OH + \underbrace{\begin{array}{c} O=CH-CH_2 \\ HO.\dot{C}O \end{array}}_{\text{Malonic aldehyde-acid.}} = \underbrace{C_6H_4{<}\begin{array}{l} CH=CH \\ O \;\; -\dot{C}O \end{array}}_{\text{Cumarin.}} + H_2O.$$

A. Monobasic Aromatic Acids.

(See table, p. 446.)

Constitution and *Isomers.* The cases of isomerism in the aromatic acids are easy to tabulate. An isomer of benzoic acid is neither theoretically possible nor actually known. Carboxylic acids of the formula $C_8H_8O_2$ may however be derived from toluene by the entrance of carboxyl either into the benzene nucleus or into the side chain, thus:

$C_6H_4(CH_3)(CO_2H)$	$C_6H_5.CH_2.CO_2H$
(3) Toluic acids.	Phenyl-acetic acid.

The behaviour of these acids upon oxidation yields proof of their constitution, the former going into the phthalic acids and the latter into benzoic.

Of acids $C_9H_{10}O_2$, a large number of isomers are already known (see table). Hydrocinnamic acid and hydratropic acid are phenyl-propionic acids, the former β- and the latter α-, corresponding to the lactic acids; the isomeric relations of the fatty acids thus repeat themselves here also. The α-xylic acids, $C_6H_4{<}\begin{array}{l} CH_3 \\ CH_2-CO_2H \end{array}$, and the ethyl-benzoic acids, $C_6H_4{<}\begin{array}{l} C_2H_5 \\ CO_2H \end{array}$, stand in the same relation to each other as aceto-acetic acid, $CH_3-CO-CH_2-CO_2H$, does to propionyl-formic acid, $C_2H_5-CO-CO_2H$, and they all yield phthalic acids upon oxidation. Lastly, mesitylenic acid and its isomers are dimethyl-benzoic acids, and are oxidizable to benzene-tri-carboxylic acids.

[Continued on p. 448.

Summary of the Monobasic

	1. Monatomic saturated Acids.		M.Pt.
C_7	Benzoic acid, ...	$C_6H_5-CO_2H$	121°
$C_8H_8O_2$	Phenyl-acetic acid, ...	$C_6H_5-CH_2-CO_2H$	76°
$C_8H_8O_2$	*o*-, *m*-, *p*-Toluic acids, ...	$C_6H_4<^{CH_3}_{CO_2H}$ { *o*- / *m*- / *p*-	102° / 110° / 180°
$C_9H_{10}O_2$	Hydrocinnamic acid, ...	$C_6H_5-CH_2-CH_2-CO_2H$	49°
$C_9H_{10}O_2$	Hydratropic acid, ...	$C_6H_5-CH<^{CH_3}_{CO_2H}$	liq.
$C_9H_{10}O_2$	α-Xylic acids, ...	$C_6H_4<^{CH_3}_{CH_2-CO_2H}$ { *o*- / *m*- / *p*-	89° / 61° / 91°
$C_9H_{10}O_2$	Ethyl-benzoic acid, ...	$C_6H_4<^{C_2H_5}_{CO_2H}$ { *o*- / *p*-	68° / 112°
$C_9H_{10}O_2$	Mesitylenic acid, . (1 : 3 : 5)	$C_6H_3<^{(CH_3)_2}_{CO_2H}$ *	166°
$C_9H_{10}O_2$	Xylic acid, . . . (1 : 2 : 4)		126°
$C_9H_{10}O_2$	Paraxylic acid, . . (1 : 3 : 4)		163°
C_{10}	Cumic acid, . . . (1 : 4, iso-)	$C_6H_4<^{C_3H_7}_{CO_2H}$	116°
	etc.		

2. Monatomic unsaturated Acids.

$C_9H_8O_2$	Cinnamic acid, ...	$C_6H_5-CH=CH-CO_2H$	133°
$C_9H_8O_2$	Atropic acid, ...	$C_6H_5-C<^{CH_2}_{CO_2H}$	106°
C_9	Phenyl-propiolic acid, . . .	$C_6H_5-C\equiv C-CO_2H$	136°

6. Unsaturated Phenolic Acids.

$C_9H_8O_3$	Cumaric acid (*o*-, *p*-), ...	$C_6H_4(OH)-CH=CH-CO_2H$ { *o*- / *p*-	208° / 206°
	etc.		

* 1 : 3 : 5, etc. ; CO_2H in position 1.

Aromatic Acids.

3. Diatomic saturated Phenolic Acids.		M.Pt.
$C_7H_6O_3$ { Salicylic acid (1 : 2) ; *m*-, *p*-Oxybenzoic acids . . .	$C_6H_4<^{OH}_{CO_2H}$ { *o*- ; *m*- ; *p*-	155° ; 200° ; 210°
[Anisic acid (1 : 4), ...	$C_6H_4(O.CH_3).CO_2H$]	184°
C_8 {Oxy-toluic acids, ... etc.	$C_6H_3(CH_3)<^{OH}_{CO_2H}$	—
C_9 { Hydro-para-cumaric acid (1 : 4),	$C_6H_4<^{OH}_{CH_2-CH_2-CO_2H}$	128°
(Tyrosine (1 : 4), ... etc.	$C_6H_4<^{OH}_{CH_2-CH<^{NH_2}_{CO_2H}}$	—

4. Diatomic saturated Alcohol- and Ketone-Acids.

C_8 {Mandelic acid, ...	$C_6H_5-CH(OH)-CO_2H$	118°
C_9 {Tropic acid, ...	$C_6H_5-CH<^{CH_2.OH}_{CO_2H}$	117°
C_8 {Benzoyl-formic acid, ...	$C_6H_5-CO-CO_2H$	65°
C_9 {Benzoyl-acetic acid, ...	$C_6H_5-CO-CH_2-CO_2H$	103°

5. Tri- and polyatomic Phenolic Acids.

C_7 {Protocatechuic acid (1 : 3 : 4) .	$C_6H_3(OH)_2(CO_2H)$	199°
[Vanillic acid, ...	$C_6H_3(OH)(O.CH_3)(CO_2H)$]	207°
C_8 {Orsellinic acid, ...	$C_6H_2(CH_3)(OH)_2(CO_2H)$	176°
C_7 { Gallic acid, ...	$C_6H_2(OH)_3(CO_2H)$	222°
[Tannin, ...	$C_{14}H_{10}O_9$]	—
Quinic acid, ...	$C_6H.(H_6)(OH)_4(CO_2H)$	162°
etc.		

As is easily seen, the following acids are isomeric with cumic acid (*p*-isopropyl-benzoic acid), $C_{10}H_{12}O_2$: first, *p*-normal-propyl-benzoic acid and the corresponding *o*- and *m*-compounds, then the methyl-ethyl-benzoic acids, trimethyl-benzoic acids, phenyl-butyric acids, and so on.

As instances of isomers among the unsaturated acids we may take cinnamic and atropic acids (analogous to β- and α-chlor-acrylic acids, p. 183).

Further, the oxy-toluic acids, $C_6H_3(CH_3)(OH)(CO_2H)$, are isomeric with mandelic acid, $C_6H_5—CH(OH)—CO_2H$, the former being oxidizable to oxy-phthalic acids, $C_6H_3(OH)(CO_2H)_2$, and the latter to benzoic acid; the hydrocumaric acids, $C_9H_{10}O_3$, are likewise isomeric with tropic acid. The first-named go into oxy-benzoic acids upon oxidation and the last into benzoic.

Differences are apparent, *e.g.* in respect to reducibility, according as the carboxyl is linked directly to the nucleus or to a side chain; the amides of the respective acids are in the former case changed by reduction into the corresponding alcohols, but not in the latter (just as in the fatty series). Cf. B. **24**, 173.

1. Monatomic Saturated Acids.

Benzoic Acid.

Benzoic acid, $C_6H_5.CO_2H$, was discovered in gum benzoïn in 1608 and prepared from urine by *Scheele* in 1785. Its composition was established by *Liebig* and *Wöhler's* classical researches in 1832. It occurs in nature in gum benzoïn, from which it may be obtained by sublimation ("Acidum benzoicum ex resina"); also in dragon's blood (a resin), in Peru and Tolu balsams, in castoreum and in cranberries. It is present in the urine of horses in combination with glycocoll as hippuric acid, from which it results upon boiling with hydrochloric acid ("acidum benzoicum ex urina"). It is obtained on the large scale ("ac. benz. e toluole") as a bye-product in the manufacture of oil of bitter almonds from benzyl chloride or benzal chloride. The acid may also be got by heating benzo-tri-chloride with water to a somewhat high temperature:

$$C_6H_5.CCl_3 + 2H_2O = C_6H_5.CO_2H + 3HCl.$$

Benzoic acid is also present in coal tar. It crystallizes in colourless glancing plates or flat needles, sublimes readily and is volatile with steam, its vapour having a peculiar irritating odour and giving rise to coughing. M. Pt. 121°, B. Pt. 250°. It is readily soluble in hot water but only slightly in cold.

When heated with lime, it is decomposed into benzene and carbon dioxide. It is used in medicine and in the manufacture of aniline blue. Some of its salts crystallize beautifully, *e.g.* calcium benzoate, $(C_6H_5.CO_2)_2Ca + 3H_2O$, in glancing prisms or needles.

From partially or wholly hydrogenized benzene there are derived:—the **Dihydro-benzoic acids**, of which five are theoretically possible, according to the position of the double linkings; the **Tetrahydro-benzoic acids**, of which three are possible and two actually known (A. **271**, 231); and a **Hexahydro-benzoic acid** (*hexa-naphthene-carboxylic acid*), which is found in the petroleum from Baku, and which can also be prepared from benzoic acid.

Ethers, Anhydrides, Amides, etc., of Benzoic Acid.

The ethers, *e.g.* **Methyl benzoate**, $C_6H_5.CO_2(CH_3)$, B. Pt. 199°, and **Ethyl benzoate**, $C_6H_5.CO_2(C_2H_5)$, B. Pt. 213°, are prepared as given on p. 188 (by means of HCl), and are liquids of pleasant aromatic odour which boil for the most part without decomposition.

They are also produced by shaking an aqueous solution of the alcohol with benzoyl chloride and caustic soda (*Schotten; Baumann*). They frequently serve for the recognition and estimation of alcohols.

Benzyl benzoate, $C_6H_5.CO_2.(CH_2.C_6H_5)$, is present in the balsams of Peru and Tolu (from Myroxylon).

Benzoyl chloride, $C_6H_5.CO.Cl$ (*Liebig* and *Wöhler*), which can be obtained by acting upon the acid with PCl_5, is the complete analogue of acetyl chloride but more stable than the latter, since it is only slowly saponified by cold water, although quickly by hot. B. Pt. 194°. It is prepared technically by chlorinating benzoic aldehyde.

Benzoyl cyanide, $C_6H_5.CO.CN$ [from benzoyl chloride and $Hg(CN)_2$], serves for the synthesis of benzoyl-formic acid (p. 460).

Benzoic anhydride, $(C_6H_5.CO)_2O$ (*Gerhardt*), is exactly analogous to acetic anhydride. It crystallizes in prisms insoluble in water, boils without decomposition and becomes hydrated on boiling with water. M. Pt. 39°.

Benzamide, $C_6H_5.CO.NH_2$, exactly corresponds with acetamide and is easily prepared from benzoyl chloride and ammonia or ammonium carbonate. It forms lustrous mother-of-pearl plates of 130° M. Pt., boils without decomposition and is readily soluble in hot water.

The amido-hydrogen of benzamide may be substituted by alcohol radicles such as phenyl, etc. with the formation *e.g.* of **Benzanilide**, $C_6H_5.CO.NHC_6H_5$,

the anilide of benzoic acid, a compound which can be readily prepared from aniline and benzoic acid. It crystallizes in colourless plates, M. Pt. 158°, distils unchanged, and is in fact the complete analogue of acetanilide.

Thio-benzamide, $C_6H_5—CS.NH_2$, is obtained by the union of benzo-nitrile with hydrogen sulphide, or by heating benzylamine with sulphur. Yellow needles.

Benzoyl-hydrazine, $C_6H_5—CO—NH—NH_2$, is a compound from which hydrazoic acid, N_3H, can be prepared, seeing that it is transformed by nitrous acid into **Benzoyl-azimide**, $C_6H_5—CO—N\langle{}^{N}_{N}\|$, which yields benzoic and hydrazoic acids on saponification. Cf. *Curtius*, B. 23, 3023.

Metallic derivatives of benzamide are also known, *e.g.* **Benzamide-silver** (see Acetamide).

Hippuric acid, *benzamido-acetic acid*,

$$C_9H_9NO_3, = \begin{array}{l} CH_2—NH—CO—C_6H_5 \\ \cdot \\ CO_2H \end{array},$$ is an amido-derivative of benzoic acid, being derived from the latter and glycocoll (amido-acetic acid); it may be prepared *e.g.* by heating benzoic anhydride with glycocoll (B. 17, 1663). Hippuric acid is present in the urine of horses and of other herbivora. When benzoic acid or toluene is taken internally, it is voided in the form of hippuric acid. It crystallizes in rhombic prisms, sparingly soluble in cold water but readily in hot, decomposes on being heated, and forms salts, ethers, nitro-derivatives, etc.

Chloro-, Nitro- and Sulph-amido-benzoic Acids.

The hydrogen of benzoic acid is replaceable by halogen with the formation *e.g.* of **Chloro-benzoic acid**, $C_6H_4Cl.CO_2H$. In such formation of mono-substitution products the halogen takes up the meta-position to the carboxyl. Nitric acid (especially a mixture of nitric and sulphuric acids) nitrates readily, *m*-**Nitro-benzoic acid** being chiefly produced, together with a smaller quantity of the ortho- and a very little of the para-acid.

The Amido-benzoic acids, $C_6H_4<^{NH_2}_{COOH}$, which result from the reduction of the nitro-acids by tin and hydrochloric acid, etc., are at the same time bases and acids, and therefore similar to glycocoll in chemical character; they combine with hydrochloric acid, hydrochloric acid and platinic chloride, etc., as well as with bases. With regard to their constitution, cf. p. 340.

With nitrous acid they yield diazo-benzoic acids, $C_6H_4<^{N=N}_{CO_2}>$, which correspond to the diazo-benzene-sulphonic acids.

o-**Amido-benzoic acid** is also obtained from phthal-imide by the *Hofmann* reaction (cf. Amides, behaviour of, par. 5), and by the oxidation of indigo with manganese dioxide and caustic soda, and is often termed **Anthranilic**

acid; it forms (in contradistinction to the *m*- and *p*-acids) an intramolecular anhydride, **Anthranil**, $C_6H_4\langle{}^{CO}_{NH}\rangle$.

Diamido-benzoic acids, $C_6H_3(NH_2)_2(CO_2H)$, (see p. 346). The **Diazo-benzoic nitrates**, $C_6H_4\langle{}^{N=N-NO_3}_{CO_2H}$, possess in full degree the characteristics of the diazo-compounds already described, and show the same transformations; they yield benzoic acid when boiled with alcohol, oxy-benzoic acid with water, and iodo-benzoic acid with hydriodic acid, etc.

Diazo-amido-compounds are also known.

The **Sulpho-benzoic acids**, $C_6H_4(SO_3H)(CO_2H)$, are dibasic acids.

One of the ammonia derivatives of *o*-sulpho-benzoic acid is that eminently sweet substance, the so-called "**Saccharine**," $C_6H_4\langle{}^{SO_2}_{CO}\rangle NH$, *i.e.* *o*-sulpho-benzoic imide, or *o*-benzoyl sulphone-imide, an imide comparable with succinimide. It is a white crystalline powder, almost 300 times as sweet as cane sugar, and is used to some extent in place of the latter.

Benzo-nitrile.

Benzo-nitrile, C_6H_5CN (cf. p. 441), is an oil which smells like oil of bitter almonds and boils at 191°. It is prepared either by the action of PCl_5 upon benzamide (p. 198), or by distilling benzoic acid with ammonium sulphocyanide. It possesses all the properties of a nitrile, combining slowly with nascent hydrogen to benzylamine, readily with halogen hydride to imido-chloride, with amines to amidines (p. 200; cf. A. **192**, 1), with hydroxylamine to amidoximes (p. 201), and so on.

Acids, $C_8H_8O_2$.

1. The three **Toluic acids**, $C_6H_4(CH_3)(CO_2H)$, can be prepared from the three xylenes. *p*-**Toluic acid** is obtained from *p*-toluidine, by transforming it—according to the *Sandmeyer* reaction—into *p*-cyano-toluene and saponifying the latter (A. **258**, 9). Isomeric with them is:

2. **Phenyl-acetic acid**, *a-toluic acid*, $C_6H_5.CH_2.CO_2H$ (*Cannizaro*, 1855). This acid differs characteristically from its isomers by its behaviour upon oxidation (see p. 445). It results synthetically from benzyl chloride and potassium cyanide, **Benzyl cyanide**, $C_6H_5.CH_2.CN$ (B. Pt. 232°), being formed as intermediate product; it crystallizes in lustrous plates, M. Pt. 76°, B. Pt. 262°.

It is capable of undergoing substitution either in the benzene nucleus or in the side chain. In the latter case there are formed compounds such as:

Phenyl-chlor-acetic acid, $C_6H_5—CHCl—CO_2H$, and:

Phenyl-amido-acetic acid, $C_6H_5—CH(NH_2)—CO_2H$, compounds which possess precisely the same character as monochlor-acetic and amido-acetic acids. Isomeric with phenyl-amido-acetic acid are the three **Amido-phenyl-acetic acids**, $C_6H_4(NH_2)—CH_2—CO_2H$, of which the o-acid is interesting on account of its close relation to the indigo group. It does not exist in the free state but goes into an intramolecular anhydride, oxindole (p. 472), when set free, thus:

$$C_6H_4{<}^{NH_2}_{CH_2—CO_2H} = C_6H_4{<}^{NH}_{CH_2}{>}CO + H_2O.$$

Such a formation of intramolecular anhydride is of very frequent occurrence in ortho-compounds of this kind, in contradistinction to the *m*- and *p*-compounds (see Indole). Theoretically it may take place in the above instance in two different ways, viz., either by the elimination of a hydrogen atom of the amidogen together with OH, or of both of the amidogen H-atoms with O. These two cases are distinguished by *Baeyer* as "Lactame formation" and "Lactime formation."

Oxindole is a lactame, while isatin, $C_6H_4{<}^{N}_{CO}{>}C.OH$ (p. 471), is a lactime of *o*-amido-phenyl-glyoxylic acid (p. 460).

Both lactames and lactimes contain hydrogen which is readily replaceable; in the former case it is present in the amido-group and in the latter in the hydroxyl.

If the compounds which result from the replacement of hydrogen by alkyl are very stable, the alkyl in them is linked to the nitrogen and they are *derivatives of the lactames*; *if on the contrary they are easily* saponifiable, the alkyl is linked to oxygen and they are ethers of the lactimes.

Acids, $C_9H_{10}O_2$.

1. **Dimethyl-benzoic acids**, *xylene-carboxylic acids*, $C_6H_3(CH_3)_2(CO_2H)$. Of these six are possible and four are known.

Mesitylenic acid, $(CO_2H : CH_3 : CH_3 = 1:3:5)$, results from the oxidation of mesitylene, and **Xylic** and **Para-xylic** acids from that of pseudo-cumene. Isomeric with them are:

2. The **Phenyl-propionic acids**, $C_6H_5—C_2H_4—CO_2H$. These may be either α- or β-derivatives of propionic acid.

β-Phenyl-propionic acid or Hydrocinnamic acid,

$C_6H_5—CH_2—CH_2—CO_2H$, results from the action of sodium amalgam upon cinnamic acid and from the decay of albuminous matter. Fine needles; M. Pt. 48°, B. Pt. 280°.

Many substitution products etc. of this acid are known, among which may be mentioned *o*-**Nitro-cinnamic dibromide**, $C_6H_4<^{NO_2}_{CHBr—CHBr—CO_2H}$, a compound nearly related to indigo (p. 470); further, **Phenyl-α-amido-propionic acid** (phenyl-alanine), $C_6H_5—CH_2—CH(NH_2)—CO_2H$, and **Phenyl-β-amido-propionic acid**, $C_6H_5—CH(NH_2)—CH_2—CO_2H$, both of which can be prepared synthetically, the former being likewise produced by the decay of albumen and by the germination of (*e.g.*) Lupinus luteus.

The isomeric *o*-**Amido-hydrocinnamic acid**, $C_6H_4<^{NH_2}_{C_2H_4—CO_2H}$, is not stable, but goes immediately into its lactame, hydro-carbostyril, C_9H_9ON, a quinoline derivative.

Hydratropic acid, *a-Phenyl-propionic acid*, $C_6H_5—CH(CH_3)—CO_2H$, is obtained—as its name implies—by the addition of hydrogen to atropic acid. It is liquid and volatile with steam.

Acids, $C_{10}H_{12}O_2$.

Among these may be mentioned **Cumic acid** or *p-isopropylbenzoic acid*, $C_6H_4(C_3H_7)(CO_2H)$, which is obtained by oxidizing Roman oil of cumin with permanganate of potash; (this oil contains—in addition to cymene—its aldehyde, cumic aldehyde). It also results from the oxidation of cymene in the animal organism, the propyl group being here changed into the isopropyl one. It crystallizes in plates, boils without decomposition, and yields cumene when distilled with lime.

The isomeric **normal Propyl-benzoic acid** has also been prepared (see p. 364).

2. Monatomic unsaturated acids.

1. Cinnamic acid, $C_9H_8O_2$, $= C_6H_5—CH=CH—CO_2H$, (*Trommsdorf*, 1780), occurs in Peru and Tolu balsams and also in storax, and may be prepared as given at p. 444. It crystallizes in needles or prisms, readily soluble in hot water; M. Pt. 133°, B. Pt. 300°. When fused with potash, it is split up into

benzoic and acetic acids, going into the former also upon oxidation. It yields salts, compound ethers, etc.; also HCl-, HBr-, HI-, ClOH-, Br_2- etc. addition compounds, *e.g.* cinnamic dibromide (phenyl-dibromo-propionic acid), $C_6H_5—CHBr—CHBr—CO_2H$. Further, the hydrogen in the benzene nucleus may be replaced by Cl, Br, NO_2, NH_2, etc.

Theoretically, a second *stereo-isomeric* cinnamic acid should exist, according to the formulæ:—

$$\text{(I.)}\ \begin{array}{c} H—C—C_6H_5 \\ \| \\ H—C—CO_2H \end{array} \quad \text{and} \quad \text{(II.)}\ \begin{array}{c} C_6H_5—C—H \\ \| \\ H—C—CO_2H \end{array}$$

(cf. pp. 24 and 180). As a matter of fact an **Allo-cinnamic acid** (M. Pt. 68°; present in coca-leaves) is known, which is readily convertible into ordinary cinnamic acid, and which can be prepared from phenyl-propiolic dibromide; it probably corresponds therefore to formula (I.) and cinnamic acid to formula (II.). Besides these there is a dimorphous (physically isomeric) form, "*Iso-cinnamic acid,*" M. Pt. 57°, which changes slowly into allo-cinnamic acid on standing (*Liebermann*, B. **23**, **24**, **25**, 89, 950; also B. **23**, 3130).

o- and *p*-**Nitro-cinnamic acids**, $C_6H_4{<}^{NO_2}_{CH=CH—CO_2H}$, the first of which is of importance on account of its relation to indigo, result from the nitration of cinnamic acid. On reduction the former yields *o*-**Amido-cinnamic acid**, $C_6H_4{<}^{NH_2}_{CH=CH—CO_2H}$ (fine yellow needles), which readily gives up water and goes into its lactime carbostyril (α-oxy-quinoline), $C_6H_4{<}^{CH=C(OH)}_{N=CH}$.

The radicle of cinnamic acid, *i.e.* ($C_6H_5—CH=CH—CO$), is termed "cinnamyl," and the group ($C_6H_5—CH=CH$), "cinnamenyl."

2. **Atropic acid**, $C_9H_8O_2$, is a decomposition product of atropine. It crystallizes in monoclinic tables and can be distilled with steam. It breaks up into formic and α-toluic acids when fused with potash, this decomposition taking place at the point of the double bond, as in the cases of cinnamic acid and the unsaturated acids of the fatty series.

3. (γ)-**Phenyl-isocrotonic acid**, $C_6H_5—CH=CH—CH_2—CO_2H$, results upon heating benzaldehyde with sodium succinate and acetic anhydride (*W. H. Perkin, sen.*):

$$C_6H_5—CHO + \begin{array}{l} CH_2—CO_2H \\ | \\ CH_2—CO_2H \end{array} - H_2O = \underbrace{C_6H_5—CH{=}\begin{array}{l} C—CO_2H \\ | \\ CH_2—CO_2H \end{array}}_{\text{Intermediate product.}}$$

$$= C_6H_5—CH{=}\begin{array}{l} CH \\ | \\ CH_2—CO_2H \end{array} + CO_2.$$

It is of interest on account of its conversion into α-naphthol upon boiling (see p. 473).

4. **Phenyl-propiolic acid**, $C_9H_6O_2$, = $C_6H_5—C{\equiv}C—CO_2H$ (*Glaser*, 1870), is formed by the addition of bromine to ethyl cinnamate and subsequent heating of the dibromide, $C_6H_5—CHBr{=}CHBr—CO_2C_2H_5$, so obtained with alcoholic potash (just as ethylene is converted by bromine into ethylene bromide, and the latter decomposed into acetylene by potash). It crystallizes in long glancing needles which can be sublimed; M. Pt. 136–137°. When heated with water to 120°, it breaks up into CO_2 and phenyl-acetylene (p. 366). It can be reduced to hydrocinnamic acid and transformed into benzoyl-acetic acid.

o-**Nitro-phenyl-propiolic acid**, $C_6H_4{<}^{NO_2}_{C{\equiv}C—CO_2H}$ (*Baeyer*), is prepared in a manner analogous to that just given, viz., by the addition of Br_2 to ethyl *o*-nitro-cinnamate and treatment of the resulting bromide with alcoholic potash, (A. 212, 240). It is employed technically on account of its relation to indigo (see p. 470). It breaks up into CO_2 and *o*-nitro-phenyl-acetylene upon boiling.

3. Diatomic (saturated) Phenolic Acids.

For *modes of formation*, see p. 442. These acids may also be obtained by the oxidation of the homologues of phenol and of the oxy-aldehydes, which is effected, among other methods, by fusing with alkalies.

The phenolic acids form salts both as carboxylic acids and as phenols, salicylic acid, for instance, the two following classes:

$$C_6H_4{<}^{OH}_{CO_2Na} \quad \text{and} \quad C_6H_4{<}^{ONa}_{CO_2Na}.$$

"Neutral" and "Basic" sodium salicylate.

The first of these two salts is not decomposed by CO_2, while the second, as the salt of a phenol, is decomposed by it and

converted into the first. The diatomic phenolic acids behave therefore like monobasic acids towards sodium carbonate. When both of the hydrogen atoms are replaced by alkyl, there are formed compounds such as $C_6H_4(OC_2H_5).CO_2(C_2H_5)$, which are only half saponified upon being boiled with potash [*e.g.* to $C_6H_4(OC_2H_5).CO_2H$]. Such ether-acids possess completely the character of monobasic acids, their alcoholic radicle being only eliminated by hydriodic acid at a rather high temperature. (Cf. p. 417.)

The *o*-oxy-acids ($CO_2H : OH = 1 : 2$) are, in contradistinction to their isomers, volatile with steam, give a violet or blue colouration with ferric chloride, and are readily soluble in cold chloroform.

The *m*-oxy-acids are more stable than the *o*- and *p*-compounds; while most of the latter break up into carbon dioxide and phenols when quickly heated or when acted on by hydrochloric acid at 220°, the former remain unaltered.

The phenolic acids are much more easily convertible into substitution products, etc. by halogens or nitric acid than the monatomic monobasic acids, just as the phenols are far more readily attacked than the benzene hydrocarbons.

Oxy-benzoic acids, $C_6H_4(OH)CO_2H$.

Salicylic acid, *o-oxybenzoic acid*, ($CO_2H : OH = 1 : 2$).

This acid was discovered by *Piria* in 1839.

Occurrence. In the blossom of Spiræa Ulmaria, as methyl ether in oil of winter green, etc.

Formation. By the oxidation of saligenin; by fusing cumarin, indigo, *o*-cresol, etc. with potash; by diazotizing *o*-amido-benzoic acid, etc., etc. For other methods, see p. 442.

Preparation. 1. By heating sodium phenate in a stream of carbonic acid at 180–220° (*Kolbe*, A. **113**, 125; **115**, 201, etc), when half of the phenol distils over and basic salicylate of sodium remains behind:

$$C_6H_5ONa + CO_2 = C_6H_4(OH).CO_2Na;$$
$$C_6H_4(OH).CO_2Na + C_6H_5.ONa = C_6H_4(ONa).CO_2Na + C_6H_5.OH$$

Should potassium phenate be used instead of the sodium compound, salicylic acid is likewise formed if the temperature be kept low (150°), but the isomeric para-oxybenzoic acid at a higher temperature (220°). Neutral salicylate of potassium, $C_6H_4(OH).CO_2K$, decomposes in an analogous manner at 220° into phenol and basic potassium *p*-oxybenzoate.

2. Sodium phenate is heated with CO_2 in a closed vessel to 130°, when neutral salicylate of sodium results, (*Schmitt*, B. **20**, Ref. 302), sodium phenol-carbonate, $C_6H_5.O.CO_2Na$, being formed here as intermediate product.

Salicylic acid crystallizes in colourless four-sided monoclinic prisms, sparingly soluble in cold water but readily in hot; M. Pt. 159°. It can be sublimed, but breaks up into phenol and CO_2 when heated quickly; Fe_2Cl_6 colours the aqueous solution violet. It is an important antiseptic. It forms two series of salts (the basic calcium salt being insoluble in water), and two series of derivatives, viz.: (1) as an acid it yields chlorides, compound ethers, etc., and (2) as a phenol it yields a methyl ether, etc. *e.g.* ethyl-salicylic acid, $C_6H_4(O.C_2H_5)CO_2H$. (Cf. p. 417.)

With phenol as alcohol there results **Phenyl salicylate**, $C_6H_4<^{OH}_{CO.OC_6H_5}$, generally termed "**Salol**," a good antiseptic, which is prepared by the action of an acid chloride such as $COCl_2$ upon a mixture of salicylic acid and phenol, (B. **20**, Ref. 351). It forms colourless crystals. When its sodium salt is heated to 300°, it undergoes molecular transformation into the sodium salt of the isomeric **Phenyl-salicylic acid**, $C_6H_4<^{OC_6H_5}_{CO_2Na}$ (B. **21**, 501). Salol is also formed by heating salicylic acid to 220°. Analogous "salols" result from other phenols.

m-**Oxybenzoic acid** is prepared by diazotizing *m*-amidobenzoic acid. It crystallizes in microscopic plates, is readily soluble in hot water, and sublimes without decomposition; Fe_2Cl_6 does not colour its aqueous solution.

p-**Oxybenzoic acid** forms monoclinic prisms ($+H_2O$); ferric chloride gives no colouration with the aqueous solution.

As a phenol it yields the methyl ether, **Anisic acid**, $C_6H_4(O.CH_3).CO_2H$, which can be prepared by treating *p*-oxybenzoic acid with methyl alcohol, potash and methyl iodide, and saponifying the dimethyl ether

at first formed; it also results from the oxidation of anisol. Beautiful rhombic prisms. In consequence of the phenolic hydroxyl having been etherified, it resembles the monobasic and not the phenolic acids, boiling—for example—without decomposition; HI and HCl break it up into *p*-oxybenzoic acid and methyl iodide or chloride. For its transformation into anisol, see p. 417.

Acids $C_8H_8O_3$.

***p*-Oxy-phenyl-acetic acid**, $C_6H_4(OH).CH_2.CO_2H$, is contained in urine and has also been noticed as a product of the decay of albumen. Flat-shaped needles. Ferric chloride colours its solution a dirty green.

Acids $C_9H_{10}O_3$.

Hydro-ortho-cumaric acid, *melilotic acid*, $C_6H_4(OH)\text{-}CH_2\text{-}CH_2\text{-}CO_2H$ (1 : 2), occurs in melilotus officinalis and results from the reduction of cumarin.

The isomeric **Hydro-para-cumaric acid** (1 : 4) is produced by the decay of **Tyrosine** (*β*-oxyphenyl-alanine),

$$C_9H_{11}NO_3, = C_6H_4(OH){-}CH_2{-}CH(NH_2){-}CO_2H\ (1:4).$$

Tyrosine, which crystallizes in fine silky needles, is found in old cheese (τυρός), in the pancreatic gland, in diseased liver, in molasses, etc., and results from albumen, horn, etc., either upon boiling these with sulphuric acid or from their pancreatic digestion or their decay.

It has been obtained synthetically, (B. **15**, 1545; A. **219**, 179). It gives a violet colouration with Fe_2Cl_6 after being sulphurated and neutralized. Its hydrochloride, $C_9H_{11}NO_3.HCl$, crystallizes in large plates.

4. Alcohol-, Ketone-, and Aldehyde-Acids.

The monobasic aromatic alcohol-acids, which possess at one and the same time the characters of acids and of true alcohols (p. 439), contain the alcoholic hydroxyl in the side chain; this hydroxyl is consequently eliminated together with the side chain when the compound is oxidized.

In behaviour they approximate very nearly to the alcohol-acids of the fatty series, as the phenylated derivatives of which they thus appear; at the same time they yield, as phenyl derivatives, nitro-compounds, etc. (although those compounds can often not be prepared directly, on account of the ready oxidizability of the alcohol-acids). They differ from the phenolic acids in being more soluble in water, less stable, and non-volatile; as alcohols many of them give up H_2O and yield unsaturated acids (which the phenolic acids can never do), and they can be etherified by HBr, etc. with the formation of haloid-substitution acids, etc. Further, they are purely monobasic acids.

The alcohol-acids may be either primary, secondary or tertiary (see p. 224). The tertiary can sometimes be prepared directly by the oxidation of such acids $C_nH_{2n-8}O_2$ as contain a tertiary hydrogen atom ($\equiv$CH), by means of $KMnO_4$.

To the ketonic acids the corresponding reactions apply. As ketones they are reducible to alcohols, the above (secondary) alcohol-acids, and they *further react with hydroxylamine, etc.*; *as acids* they likewise form compound ethers, etc.

Polybasic alcohol-acids, etc. are of course also theoretically possible; likewise phenolic alcohol-acids (which are at the same time phenol and alcohol-acid), and so on. Some of these are known.

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1. **Mandelic acid,** *phenyl-glycollic acid,* C_6H_5–CH(OH)–CO_2H, (1835), results upon heating amygdalin with hydrochloric acid, and synthetically upon saponifying benzaldehyde-cyanhydrin, C_6H_5.CH(OH).CN, (see pp. 434 and 144). Glancing crystals, rather easily soluble in water; M. Pt. 133°.

Mandelic acid exists in several optically different modifications, viz., dextro-, lævo-, and inactive or para-mandelic acid, (cf. B. **16**, 1565 and 2721). It is comparable with lactic acid, CH_3—CH(OH)—CO_2H, yielding, like the latter, formic acid (together with benzoic) upon oxidation; hydriodic acid reduces it to phenyl-acetic acid, just as it does lactic acid to propionic.

Hydrindic acid, $C_6H_4(NH_2)$—CH(OH)—CO_2H, whose lactame is dioxindole (p. 472), is an *o*-amido-mandelic acid.

2. ***o*-Oxymethyl-benzoic acid,** $C_6H_4\!<\!\begin{smallmatrix}CH_2.OH\\CO.OH\end{smallmatrix}$, which is isomeric

readily soluble in water, alcohol and ether, and has a faintly acid and astringent taste. It gives up CO_2 and goes into pyrogallol when heated, reduces gold and silver salts, and yields a bluish-black precipitate with ferric chloride. Like pyrogallic acid, it is very readily oxidized in alkaline solution, with the production of a brown colour.

Among its isomers is **Pyrogallol-carboxylic acid** (1 : 2 : 3 : 4).

Tannin, *gallotanic acid,* $C_{14}H_{10}O_9 + 2H_2O$, is a colourless amorphous glancing mass, readily soluble in water but only slightly in alcohol, and almost insoluble in ether. It forms the chief constituent of nutgalls, and is likewise present in sumach, tea, etc. It goes into gallic acid when boiled with dilute acids, being conversely obtained from the latter, *e.g.* by means of $POCl_3$, with separation of water:

$$2C_7H_6O_5 = C_{14}H_{10}O_9 + H_2O.$$

The aqueous solution is coloured dark blue by ferric chloride. The **Mercury salt** is used in medicine. Tannin has an affinity for the animal skin and for glue, and is abstracted from its solution by these substances, the skin being thus tanned or converted into leather.

Analogous to tannin in this latter respect are a number of other tannic acids, viz. **Kino-tannic acid, Catechu-tannic acid** (in Mimosa catechu), **Morin-tannic acid** (in Morus tinctoria), **Caffetannic acid, Oak-tannic acid** (in oak bark), **Cinchona-tannic acid** (in cinchona bark), etc.; the composition of these is for the most part complicated, since the larger number of them are glucosides (p. 558), *i.e.* ethers of tannic acids with glucoses, and consequently break up into gallic acid and the sugar when boiled with dilute acids. They are characterized by their great solubility in water, harsh astringent taste, affinity for the animal skin, and also by the intense colourations they give with ferrous or ferric salts, as well as by the fact of their being precipitated by a solution of lead acetate.

Tetroxy-benzoic acids.

Quinic acid, $C_7H_{12}O_6$, which is found in quinine bark, coffee beans, etc., is a hexahydro-tetroxy-benzoic acid, $C_6H.H_6.(OH)_4CO_2H$. It crystallizes in colourless prisms and is optically active, an inactive modification being also known.

6. Unsaturated monobasic Phenolic Acids.

Oxy-cinnamic acids.

Cumaric acids, $C_6H_4<\begin{matrix}OH\\ CH=CH-CO_2H.\end{matrix}$

o-**Cumaric acid** is present in melilot (Melilotus officinalis), and can be prepared by diazotizing *o*-amido-cinnamic acid, or from salicylic acid by the *Perkin* reaction. It also results, as potassium salt, on dissolving its intra-molecular anhydride, cumarin, in concentrated potash solution. Long needles, which decompose upon fusion and are readily soluble in water and alcohol. The alcoholic solution is yellow with a green fluorescence.

Cumarin or *cumaric anhydride,* $C_6H_4<\begin{matrix}O-CO\\ CH=CH\end{matrix}$, is the aromatic principle of woodruff (Asperula odorata), and is also found in the Tonka bean and other plants. It is obtained by the elimination of H_2O from *o*-cumaric acid, *e.g.* by means of acetic anhydride. For its formation from phenol by means of malic acid etc., see p. 445. Glancing prisms, readily soluble in alcohol, ether and hot water; M. Pt. 67°, B. Pt. 290°.

With regard to isomerism in the cumaric acid series, see *Fittig,* A. **216**, 119, 170.

Dioxy-cinnamic acids.

To this group belong **Caffeic acid,**

$$C_9H_8O_4, = C_6H_3(\overset{3,4}{OH})_2-(CH=\overset{1}{C}H-CO_2H)$$

(yellow prisms, from caffetannic acid), whose mono-methyl ether is **Ferulic acid** (from asafœtida); further, the isomeric **Umbellic acid** or *p*-oxy-*o*-cumaric acid, which readily changes into the anhydride corresponding to cumarin, viz., **Umbelliferone,** $C_9H_6O_3$; this last-named compound is present in varieties of Daphne.

Related to the above is **Piperic acid**:

$$C_6H_3\left(\begin{matrix}O\\ O\end{matrix}>CH_2\right).CH=CH-CH=CH-CO_2H,$$

a decomposition product of piperine (p. 528), which crystallizes in long needles.

Trioxy-cinnamic acids.

Æsculetin, $C_6H_2(OH)_2<\begin{matrix}O\ -CO\\ CH=\dot{C}H\end{matrix}$, and its isomeride **Daphnetin** are dioxy-cumarins, their glucosides (*Æsculin* and Daphnin) occurring respectively in the horse chestnut and in Daphne varieties. Like the dioxy-cinnamic acids they may also be prepared synthetically (B. **16**, 2119; **17**, 2187, etc.).

B. Dibasic Acids.

The dibasic acids occupy exactly the same position in the aromatic series as the dibasic acids $C_nH_{2n-2}O_4$ do in the fatty; they form two series of each derivative (compound ethers, chlorides, amides, etc.). The two carboxyl groups, which according to theory they contain, may either both be in the nucleus or in the side chain or chains, or be divided between them. Dibasic phenolic acids can of course occur here also.

Benzene-dicarboxylic acids, $C_6H_4(CO_2H)_2$.

1. **Phthalic acid**, $C_6H_4(CO_2H)_2$ (1 : 2), (*Laurent*, 1836), results when any *o*-di-derivative of benzene, which contains two carbon side chains, is oxidized by HNO_3 or $KMnO_4$, but not CrO_3 (cf. p. 359); it is formed in especial by the oxidation of naphthalene by nitric acid, and also of anthracene derivatives. In preparing it on the large scale the naphthalene is first converted into its tetra-chlor-addition product, $C_{10}H_8Cl_4$, and this then oxidized. It crystallizes in short prisms or plates, M. Pt. 213°, readily soluble in water, alcohol and ether. When heated above its melting point, it goes into the anhydride (see below). It loses one mol. CO_2 when heated with a little lime, and two mols. when heated with excess, yielding benzoic acid or benzene. Chromic acid disintegrates it completely, while sodium amalgam converts it into dihydro-, tetrahydro-, and finally hexahydro-phthalic acid (see below). Its barium salt, $C_6H_4(CO_2)_2Ba$, is difficultly soluble in water.

Phthalic anhydride, $C_6H_4<{CO \atop CO}>O$, crystallizes in magnificent long prisms which can be sublimed; M. Pt. 128°, B. Pt. 284°. It is used in the preparation of eosin dyes (see Fluoresceïn).

Phthalimide, $C_6H_4<{CO \atop CO}>NH$, corresponds to succinimide in many respects.

The chloride, **Phthalyl chloride**, which results from the action of PCl_5 upon the acid, appears strangely enough not to have the constitution $C_6H_4(COCl)_2$ but that of $C_6H_4<{CCl_2 \atop CO}>O$, as it yields, for instance, phthalo-phenone, $C_6H_4<{C(C_6H_5)_2 \atop CO}>O$, with benzene and Al_2Cl_6. Sodium amalgam transforms it into phthalide.

2. **Isophthalic acid** (1:3) crystallizes in fine long needles from hot water, in which it is only sparingly soluble; it sublimes without forming an anhydride. It is prepared from *m*-xylene. The barium salt is readily soluble in water.

3. **Terephthalic acid** (1:4) results from th[illegible] *p*-xylene, cymene, etc., and especially of oi[illegible]tine or oil of cumin. It forms a powder almost i[illegible]ble in alcohol and water, and sublimes unchanged. For its p[illegible]n *p*-toluic acid is oxidized by permanganate of potash (A. [illegible]). The barium salt is only sparingly soluble.

A. Baeyer's researches (A. **245**, **251**, **258**, **266**, and **269**) have int[illegible] us to a whole series of hydro-phthalic acids. The isomers amon[illegible]m differ from one another either by the position of the double bo[illegible] the ring (*structural isomerism*), or by the spacial arrangement of th[illegible]oxyl groups with respect to the ring (*stereo-isomerism*). This latter [illegible]erism corresponds to that of fumaric and maleic acids, and a distinction is therefore made here also between a *trans*- and a *cis*-form (cf. A. **245**, 130). Exactly the same applies to the hydro-terephthalic acids.

Of the **Hydro-phthalic acids** (A. **269**, 147) there are now known:—Five *Dihydro-acids* (two of which are stereo-isomeric), four *Tetrahydro-acids* (of which two again are stereo-isomeric), and two *Hexahydro-acids* (which are stereo-isomers). Of the **Hydro-terephthalic acids** (A. **258**, 1), five *Dihydro-*, three *Tetrahydro-*, and two *Hexahydro-acids* are known, two in each group being stereo-isomeric.

The following principles, deduced from the fatty series, have mainly served for determining the position of the double bond in these compounds:—(1) When bromine substitutes in a carboxylic acid it takes up the α-position to the carboxyl (*i.e.* it is attached in the benzene nucleus to the same carbon atom to which the carboxyl is linked). (2) If two bromine atoms stand in the *ortho*-position to one another in a hydrogenized benzene nucleus, they are eliminated without replacement by the action of zinc dust and glacial acetic acid; whereas, if they stand in the *para*-position, they are replaced by hydrogen. Further, just as in the case of the unsaturated acids of the fatty series, the change of one acid into a structural isomer—upon boiling with alkali—has frequently been observed here, through the "wandering" of a double bond in the direction of a carboxyl group. *The stereo-isomeric modifications are easily transformed one into the other.*

The relations existing between the five known dihydro-phthalic acids may be taken as an example. When phthalic acid is reduced by sodium amalgam in presence of acetic acid, trans- Δ 3, 5-dihydro-phthalic acid is produced, and this changes into the cis- Δ 3, 5-acid on heating with acetic anhydride (for the above nomenclature, see p. 350). Both of these yield the Δ 2, 6-dihydro-acid when warmed with alkali. When the dihydrobromide of the latter acid is treated with alcoholic potash, the Δ 2, 4-dihydro-acid results, and, lastly, the anhydride of this yields the anhydride of the Δ 1, 4-dihydro-acid when heated. All of the dihydro-phthalic acids give anhydrides with the exception of the Δ 3, 5-acid, which comports itself like fumaric acid in this respect.

The completely hydrogenized acids show great differences from the partially hydrogenized. Thus, hexahydro-terephthalic acid is exactly similar to a saturated acid of the fatty series; cold permanganate of potash has no effect upon it, while bromine substitutes (upon warming).

On the other hand, the partially hydrogenized acids comport themselves precisely like the unsaturated acids of the fatty series with an open chain. They are very readily oxidized by cold permanganate, and take up bromine or hydrobromic acid until the saturation stage of the hexa-methylene ring is reached. When two atoms of bromine are added on, these never take up the *para*-position to one another, but always the *ortho*.

The conversion of the hexahydro-acids into benzene-carboxylic acids, through the tetra- and dihydro-acids, does not proceed uniformly; in the formation of the benzene-carboxylic- from the dihydro-acids a sudden transition occurs, which manifests itself in an immediate change in chemical character as well as in physical constants.

It is from these researches that the assumptions developed on p. 349 with regard to the special constitution of the benzene ring in those compounds are based. The observations made upon the oxidation of the hydrophthalic

acids have further helped towards the establishment of *para*-linkings in the benzene-carboxylic acids (see *A*. 269, 179).

Of the **Hydro-isophthalic acids**, one hexahydro-acid has been obtained by the reduction of isophthalic acid (B. **25**, 1040). The same acid also results synthetically (along with a stereo-isomer) from derivatives of the fatty series (p. 354). This constitutes a further proof that the hexahydro-benzene-carboxylic acids are nothing more than hexa-methylene derivatives.

A large number of substitution products of the phthalic acids are known, *e.g.* **chloro-** and **bromo-phthalic acids** (which are used in the eosin industry), nitro-, amido-, oxy- and sulpho-phthalic acids, etc.

Homologous are the:

Homo-phthalic acids, $C_6H_4<\begin{matrix}CH_2-CO_2H\\CO_2H\end{matrix}$, and:

o-**Hydrocinnamo-carboxylic acid**, $C_6H_4<\begin{matrix}CH_2-CH_2-CO_2H\\CO_2H\end{matrix}$, which results from the oxidation of tetrahydro-naphthalene, and which corresponds to an:

o-**Cinnamo-carboxylic acid**, $C_6H_4(CO_2H)(CH=CH-CO_2H)$.

Oxy-phthalic Acids.

The six **Oxy-phthalic acids**, $C_6H_3(OH)(CO_2H)_2$, are of theoretical interest (cf. p. 346).

Dioxy-terephthalic acid, *hydroquinone-p-dicarboxylic acid*, $C_8H_6O_6$, $= C_6H_2(OH)_2(CO_2H)_2$, in which both the hydroxyls and the carboxyls are respectively in the *p*-position to one another, results as ethyl ester by the action of bromine upon succino-succinic ester, or of sodium ethylate upon dibromo-aceto-acetic ester. The free acid breaks up into hydroquinone and CO_2 when distilled, and is converted by nascent hydrogen into succino-succinic acid.

Succino-succinic acid, *p-dioxy-dihydro-terephthalic acid*, $C_6H_2.(H_2).(OH)_2(CO_2H)_2$, results as ethyl ester by the action of sodium upon the ethyl ester of succinic acid (see p. 354). For its constitution, see B. **22**, 2168; **24**, 2687; also A. **211**, 306; **258**, 261. The **Ethyl ester** crystallizes in triclinic prisms which melt at 126°, and dissolve in alcohol to a bright blue fluorescent liquid which is coloured cherry-red by ferric chloride. It contains two replaceable H-atoms (in the methine groups), being analogous to aceto-acetic ester. The free acid, on losing CO_2, changes into quinone tetrahydride or *diketo-hexamethylene* (p. 429), a molecular transformation taking place.

Hemipinic acid is a dimethyl ether of the isomeric pyrocatechin-*o*-dicarboxylic acid, while the half-aldehyde of the latter is Opianic acid, and the corresponding alcohol-acid is Meconinic acid, $C_6H_2(O.CH_3)_2(CO_2H)(CH_2.OH)$; all these compounds are nearly related to protocatechuic acid, and can be

prepared from narcotine. For the constitution of opianic acid, cf. also B. 19, 2275.

C. Tri- to Hexabasic Acids.

Benzene-tricarboxylic Acids, $C_6H_3(CO_2H)_3$.

1. Trimesic acid (1:3:5). From mesitylene.
2. Trimellitic acid (1:2:4). From colophonium.
3. Hemimellitic acid (1:2:3).

Phloroglucin-tricarboxylic acid, *triketo-hexamethylene-tricarboxylic acid*, $C_6H_3O_3(CO_2H)_3$, is a derivative of trimesic acid. Its tri-ethyl ester results upon heating sodio-malonic ester, $CHNa(CO_2C_2H_5)_2$ (*Baeyer*, B. 18, 3454). The free acid obtained from this by saponification yields phloroglucin by the separation of the carboxyls (p. 426).

Benzene-tetracarboxylic Acids, $C_6H_2(CO_2H)_4$.

1. **Pyromellitic acid**; 2. **Prehnitic acid**; 3. **Mellophanic acid.**

The above three acids have been prepared from mellitic acid or its hydro-derivatives by the partial separation of CO_2. They readily yield (tetra-) hydro-acids with sodium amalgam.

4. Hydroquinone- and quinone-tetracarboxylic acids. See B. 19, 516.

Benzene-pentacarboxylic Acid, $C_6H(CO_2H)_5$.

Only one modification is theoretically possible and only one is known.

Benzene-hexacarboxylic Acid, $C_6(CO_2H)_6$.

Mellitic acid, $C_{12}H_6O_{12}$, occurs in peat as aluminium salt or honey-stone, $C_{12}Al_2O_{12} + 18H_2O$, which crystallizes in octahedra, and results from the oxidation of lignite or graphite with $KMnO_4$. It forms fine silky needles of great stability. It can neither be chlorinated, nitrated nor sulphurated, but is readily reduced by sodium amalgam to **Hydromellitic acid**, $C_{12}H_{12}O_{12}$, and yields benzene when distilled with lime.

XXVI. INDIGO (OR INDOLE) GROUP.

(Cf. the arrangement of *Baeyer's* researches, which are cited below, in *R. Meyer's* "Theerfarbstoffe," *Vieweg und Sohn.*)

Indigo, which is obtained from the indigo plant (Indigofera tinctoria), and from woad (Isatis tinctoria), has been known for thousands of years as a valuable blue dye, especially for woollen fabrics. In addition to indigo blue (indigotin), commercial indigo contains indigo-gelatine, indigo-brown and indigo-red, all of which can be extracted from it by solvents. The colouring matter is not present as such in the indigo plant, but as the glucoside "**Indican**," from which it can be separated either by dilute acids or by the action of the air in presence of water.

It forms a dark blue coppery and shimmering powder or, after sublimation, copper-red prisms, insoluble in most solvents (including the alkalies and dilute acids), but dissolving to a blue solution in hot aniline and to a red one in paraffin, from either of which it may be crystallized. Its vapour is dark red. The formula $C_{16}H_{10}N_2O_2$ is confirmed by the vapour density. It is converted by reducing agents, such as ferrous sulphate and caustic soda solution or grape sugar and soda, into **Indigo white**, $C_{16}H_{12}N_2O_2$, a white crystalline powder soluble in alcohol and ether, also in alkalies (as a phenol); the alkaline solution quickly becomes oxidized by the oxygen of the air, with the separation of a blue film of indigo. It yields an acetyl compound which crystallizes in colourless needles.

Warm concentrated or fuming sulphuric acid dissolves indigo to **Indigo-mono-sulphonic** and **di-sulphonic acids**, the former of which (termed phœnicin-sulphonic acid) is difficultly soluble in water but the latter readily so; the sodium di-sulphonate is the indigo carmine of commerce. Nitric acid oxidizes indigo to isatin, while distillation with potash yields aniline, and heating with manganese dioxide and a solution of potash, anthranilic acid.

Indigo has been prepared synthetically by *Baeyer*, (B. **14**, 1741; **15**, 775, 2093, 2856; **16**, 1704, 2188, etc.).

1. *From isatin chloride.*

2. By warming *o*-nitro-phenyl-propiolic acid with (*e.g.*) grape sugar in alkaline solution:

$$2C_6H_4(NO_2)C{\equiv}C.CO_2H + 2H_2 = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O.$$

3. From *o*-nitro-phenyl-acetylene (p. 366), by converting it into *o*-dinitro-diphenyl-diacetylene, $C_6H_4(NO_2)C{\equiv}C{-}C{\equiv}C{-}C_6H_4(NO_2)$ (p. 498), treating the latter with H_2SO_4, and finally reducing.

4. By the action of dilute alkalies upon a solution of *o*-nitro-benzaldehyde in acetone:

$$2C_6H_4(NO_2)CHO + 2C_3H_6O = C_{16}H_{10}N_2O_2 + 2C_2H_4O_2 + 2H_2O.$$

There is formed as intermediate product in this reaction "*o*-nitro-phenyl-lacto-methyl-ketone," $C_6H_4(NO_2){-}CH(OH){-}CH_2{-}CO{-}CH_3$.

5. By the oxidation, etc., of indoxylic acid and indoxyl.

6. By fusing monobrom-acetanilide, $C_6H_4Br{-}NH.C_2H_3O$, with caustic alkali (*Flimm*, B. 23, 57).

7. For *Heumann's* synthesis, see B. 23, 3043; 24, 2087. Phenyl-glycocoll, $C_6H_5{-}NH{-}CH_2{-}CO_2H$ (p. 392; also B. 25, 2029), or its carboxylic acid (from monochlor-acetic and anthranilic acids) is fused with caustic alkali, the mass dissolved in water, and the resulting leuco-compound, indoxyl, oxidized by the air.

Perhaps pseudo-indoxyl is first formed here as intermediate product:

$$C_6H_3{<}^{NH}_{HO_2C}{>}CH_2 = C_6H_4{<}^{NH}_{CO}{>}CH_2 + H_2O.$$

Homologues of indigo are produced in an analogous manner, and its sulpho-acids by the action of fuming sulphuric acid upon phenyl-glycocoll.

The *constitution* of indigo is very probably:

$$C_6H_4{<}^{NH}_{CO}{>}C{=}C{<}^{NH}_{CO}{>}C_6H_4.$$

The following are isomerides of indigo: indigo red (in the indigo of commerce), indirubin (also called indigo-purpurin), and indin; the last two of these have been prepared synthetically.

There have also been prepared dichlor-, dibrom-, tetrachlor-, diethyl-, etc. substitution products of indigo, also indigo-dicarboxylic acid, (B. 12, 458).

Derivatives of Indigo.

$C_8H_5NO_2$	Isatin	$C_6H_4<^{N}_{CO}>C(OH)$
$C_8H_7NO_2$	Dioxindole	$C_6H_4<^{NH}_{CH(OH)}>CO$
C_8H_7NO {	Oxindole	$C_6H_4<^{NH}_{CH_2}>CO$
	Indoxyl	$C_6H_4<^{NH}_{C(OH)}>CH$
C_8H_7N	Indole	$C_6H_4<^{NH}_{CH}>CH$
$C_8H_6N(CO_2H)$	Indole-carboxylic acid (*e.g.* β-)	$C_6H_4<^{NH}_{C(CO_2H)}>CH$
$C_8H_6(CH_3)N$	Skatole . . . . . . (and its isomers)	$C_6H_4<^{NH}_{C(CH_3)}>CH$

1. **Isatin,** $C_6H_4<^{N}_{CO}>C(OH)$, is easily prepared by oxidizing indigo with nitric acid (*Erdmann* and *Laurent,* 1841; cf. also* B. **17**, 976). It likewise results from the oxidation of dioxindole, of oxindole (indirectly), and of indoxyl (*Baeyer*); also by boiling *o*-nitro-phenyl-propiolic acid with alkalies. It crystallizes in reddish-yellow monoclinic prisms, which are only sparingly soluble in cold water, but more readily in hot water and in alcohol to a brownish-red solution. Caustic potash dissolves it at first to a violet solution, with the formation of the compound $C_8H_4NO.OK$, but this changes into potassium isatate, $C_6H_4(NH_2)$—CO—COOK, upon warming (p. 460). Isatin is the lactime of isatic acid (*o*-amido-benzoyl-formic acid) (p. 452); for arguments in favour of the lactame formula, however, cf. B. **23**, 253.

* For its synthesis from *o*-nitro-benzoyl-formic acid, see p. 460, and for its reaction with thiophene, p. 331. **Chloro-, Bromo-** and **Nitro-isatins** are also known. As a ketone, isatin forms with ammonia **Imesatin,** $C_8H_5NO(NH)''$, by the exchange of O for NH; and with

hydroxylamine, **Isatoxime**, $C_6H_4<\substack{N\\C(=N.OH)}>C.OH$ (yellow needles), which also results from oxindole and nitrous acid. The homologous **Methyl-isatin** can be obtained from *p*-toluidine and dichlor-acetic acid, a tolyl derivative of **Methyl-imesatin** being formed here in the first instance, (B. **18**, 190). Chromic acid oxidizes isatin to **Isatoic acid** (anthranil-carboxylic acid), $C_8H_5NO_3$, $= C_6H_4<\substack{CO\\\dot{N}-CO_2H}$ (cf. p. 451).

Isatin yields a methyl ether, **Methyl-isatin**, $C_6H_4<\substack{N\\CO}>C.O.CH_3$, which is prepared from isatin-silver (a red powder) and methyl iodide, and forms blood-red crystals; it dissolves in alkali to isatic acid and methyl alcohol, *i.e.* the water abstracted in the formation of lactime is again taken up, and the methyl ether is saponified. From this reaction the above constitutional formula of isatin follows.

An isomeric compound, **Methyl-pseudo-isatin**, is derived from an unknown isomer of isatin, pseudo-isatin, $C_6H_4<\substack{NH\\CO}>CO$, the lactame of amido-benzoyl-formic acid. This results *e.g.* by the action of sodium hypobromite upon methyl-indole and subsequent boiling with alcoholic potash; since it dissolves at once in alkali to **Methyl-isatic acid**, $C_6H_4(NH.CH_3)-CO-CO_2H$, it has the constitution $C_6H_4<\substack{N(CH_3)\\CO}>CO$, (B. **17**, 559).

Isatin chloride, $C_6H_4<\substack{CO\\N}>C.Cl$ (from isatin and PCl_5), crystallizes in brown needles which are soluble in alcohol and ether with a blue colour. It goes into indigo when treated with hydriodic acid, or with zinc dust and glacial acetic acid (synthesis of indigo, *Baeyer*):

$$2C_8H_4NOCl + 2H_2 = C_{16}H_{10}N_2O_2 + 2HCl.$$

2. **Dioxindole**, $C_6H_4<\substack{CH(OH)\\NH}>CO$, is the intra-molecular anhydride of the unstable *o*-amido-mandelic acid (p. 459). It is obtained from the reduction of isatin (into which it is again easily oxidized) with zinc dust and hydrochloric acid. Readily soluble colourless prisms, M. Pt. 180°. It possesses both basic and acid properties (two H-atoms being replaceable), and forms a nitroso-compound, acetyl derivative (the acetyl being joined to the N), etc.

3. **Oxindole**, $C_6H_4<\substack{NH\\CH_2}>CO$, the lactame of *o*-amido-phenyl-acetic acid, is formed by the reduction of *o*-nitro-phenyl-acetic acid (p. 451); also by that of dioxindole with tin and hydrochloric acid. Colourless needles, M. Pt. 120°, readily

oxidizable to dioxindole, and therefore of faintly reducing character. Oxindole is at the same time an acid and a base, dissolving both in alkalies and in hydrochloric acid. Baryta water at a somewhat high temperature transforms it into *o*-amido-phenyl-acetate of barium. The imido-hydrogen is exchangeable for ethyl, acetyl, the nitroso-group, etc.

4. Isomeric with oxindole is:

Indoxyl, $C_6H_4<{NH \atop C(OH)}>CH$, which is obtained by the separation of CO_2 from indoxylic acid, from phenyl-glycocoll (p. 470), and by fusing indigo with potash, and which is often present in the urine of the carnivora as potassium indoxyl-sulphate or urine-indican, $C_8H_6N.O.(SO_3K)$. It is a thick liquid, moderately soluble in water with yellow fluorescence, and not volatile with steam.

It dissolves in concentrated hydrochloric acid to a red solution. It is very unstable, quickly becoming resinous, and readily changing into indigo when its alkaline solution is exposed to the air, or when ferric chloride is added to its solution in hydrochloric acid.

It yields a **Nitroso-compound**, $C_6H_4<{N(NO) \atop C(OH)}>CH$, of the same character as the nitrosamines, and therefore it contains an imido-group; further, its relation to indoxyl-sulphuric acid shows that it contains an alcoholic hydroxyl, from which its constitution follows.

Potassium indoxyl-sulphate is prepared synthetically by warming indoxyl with potassium pyrosulphate; it crystallizes in glancing plates and breaks up again backwards when warmed with acids.

Ethyl-indoxyl results from indoxyl by the exchange of the hydroxylic hydrogen for C_2H_5. Derivatives of the hypothetical **Pseudo-indoxyl**, $C_6H_4<{NH \atop CO}>CH_2$, are also known, some of them being convertible into indigo derivatives (*e.g.* diethyl-indigo).

Indoxylic acid, $C_6H_4<{NH \atop C(OH)}>C-CO_2H$, the carboxylic acid of indoxyl, forms white crystals, is converted into indigo by ferric chloride, and breaks up into indoxyl and CO_2 when fused. It is obtained from its ether:

Ethyl indoxylate, by fusing with soda. The latter compound, which crystallizes in thick prisms, M. Pt. 120°, also results—among other methods—from the reduction of ethyl-*o*-nitro-phenyl-propiolate with ammonium sulphide.

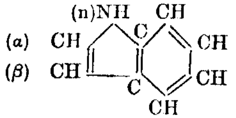
The mother substance of the whole indigo group is:

5. **Indole**, $C_6H_4<{CH \atop NH}>CH$ (*Baeyer*, 1868), which is obtained by distilling oxindole with zinc dust; by heating *o*-nitro-cinnamic acid with potash and iron filings; by the action of sodium alcoholate upon *o*-amido-chloro-styrene (from *o*-nitro-cinnamic acid $+ ClOH - CO_2$) (B. **17**, 1067):

$$C_6H_4<{NH_2 \atop CH=CHCl} + NaO.C_2H_5 = C_6H_4<{NH \atop CH}>CH + NaCl + C_2H_5OH;$$

by the pancreatic fermentation of albumen; together with skatole by fusing albumen with potash; and by passing the vapours of various anilines, *e.g.* diethyl-*o*-toluidine, through red-hot tubes, etc. It crystallizes in glancing plates, M. Pt. 52°, volatilizes readily with steam, and has a peculiar fæcal-like odour. It is weakly basic, colours a pine shaving which has been moistened with HCl cherry-red, gives a red precipitate, which consists partly of the so-called nitroso-indole, $[C_8H_6N(NO)]_2$, with N_2O_3 (a delicate reaction, see B. **22**, 1976), and yields acetyl-indole when acetylated. These last reactions show that indole contains an imido-group.

Indole may be looked upon as pyrrol which has two C-atoms in common with a benzene nucleus, as in the case of naphthalene:



$= C_6H_4<{NH \atop CH}>CH.$

A large number of derivatives spring from indole by the replacement either of the imido-hydrogen (n), or of the hydrogen atoms marked (α) and (β), or of those of the benzene nucleus. These result synthetically *e.g.* by the condensation of the aromatic primary or secondary hydrazines either with pyroracemic acid or with certain ketones or aldehydes, and treatment of the resulting hydrazones with dilute HCl or $ZnCl_2$ (*E. Fischer*, A. **236**, 116; **242**, 372); thus acetone-phenyl-hydrazone, for instance, yields α-methyl-indole, $C_6H_4<{NH \atop CH}>C—CH_3$, propyl aldehyde-phenyl-hydrazone yields skatole, and phenacyl bromide and aniline yield α-phenyl-indole. See also B. **25**, 2860.

Skatole, *β-methyl-indole*, $C_6H_4<{NH \atop C(CH_3)}>CH$, is found in fæces, and is produced together with indole *e.g.* by the decay of albumen or by fusing it with potash. Colourless plates of a strong fæcal odour, M. Pt. 95°. Nitrous acid does not colour it red. It takes up two atoms of hydrogen to form a hydro-compound. Skatole is also found in a species of wood from the East Indies.

n-Methyl-indole, $C_6H_4<\substack{N(CH_3)\\CH}>CH$, results from phenyl-methyl-hydrazine (p. 406) and pyroracemic acid, at first in the form of the carboxylic acid. It is an oil, B. Pt. 239°.

Indole-carboxylic acids, $C_8H_6N(CO_2H)$, can be synthetized, *e.g.* the *β-acid* (*together with the α-*), $C_6H_4<\substack{NH\\C(CO_2H)}>CH$, *from indole by Kolbe's* method, *i.e.* by acting on the latter with sodium and carbon dioxide.

The homologous **Skatole-carboxylic acid,** $C_9H_8N(CO_2H)$, and also **Skatole-acetic acid,** $C_9H_8N(CH_2—CO_2H)$, are produced by the decay of albuminous substances.

For the transformation of indole into quinoline derivatives, see B. **20,** 2199, 2608; **21,** 1940; **23,** 2302, 2628; **25,** Ref. 111.

Cumarone and Indazole groups.

For these see Appendix, p. 567.

The compounds of the aromatic series which have been treated of up to now are derived, with the exception of indigo, from one molecule of benzene, *i.e.* they contain one benzene nucleus. There are however a vast number of compounds known which contain two or more benzene nuclei.

1. *When two phenyl groups are joined together directly,* there results Di-phenyl, $C_6H_5—C_6H_5$ (Group XXVII.).

2. When a methylene group, *i.e.* a carbon atom, connects two phenyl groups, we obtain Diphenyl-methane, $C_6H_5—CH_2—C_6H_5$ (Group XXVIII.).

3. Should three benzene residues be joined in a similar manner to methine, Triphenyl-methane, $CH(C_6H_5)_3$, is formed (Group XXIX.).

4. Benzene nuclei may likewise be connected through two or more carbon atoms, as in Di-benzyl, $C_6H_5—CH_2—CH_2—C_6H_5$ (Group XXX.).

5. Lastly, the benzene nuclei may be so grouped together that two carbon atoms are common to two of them, as in anthracene and naphthalene, etc. (Group XXXI. etc.).

From all the hydrocarbons mentioned under the above paragraphs 1–4, homologues are derived; all of these with the exception of diphenyl (which possesses the benzene character only) have like toluene partly a benzene and partly a

methane character, and yield completely analogous derivatives, like the benzene hydrocarbons in the narrower sense of the term.

XXVII. DIPHENYL GROUP.

Summary.

1. Diphenyl, $C_6H_5—C_6H_5$, = $C_{12}H_{10}$.

p-Chloro-diphenyl	$C_{12}H_9Cl$	*p-p*-Dichloro-diphenyl	$C_{12}H_8Cl_2$
o-, *p*-Nitro-diphenyl	$C_{12}H_9(NO_2)$	{α = *p-p*-; β = *o-p*-} Dinitro-diphenyl	$C_{12}H_8(NO_2$
Amido-diphenyl	$C_{12}H_9(NH_2)$	{(*p-p*-) = Benzidine; (*o-p*-) = Diphenyline}	$C_{12}H_8(NH_2$
		Carbazole	$\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>NH$
Diphenylol	$C_{12}H_9(OH)$	Diphenols	$C_{12}H_8(OH)$
		Diphenylene oxide	$\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O$
Cyano-diphenyl	$C_{12}H_9(CN)$	Dicyano-diphenyl	$C_{12}H_8(CN)$
Diphenyl-carboxylic acid	$C_{12}H_9(CO_2H)$	Diphenyl-dicarboxylic acid	$C_{12}H_8(CO_2$

2. Phenyl-tolyls, $C_6H_5—C_6H_4.CH_3$.
3. Ditolyls, $C_6H_4(CH_3)—C_6H_4(CH_3)$, etc.
4. Diphenyl-benzene, $C_6H_4(C_6H_5)_2$.
5. Triphenyl-benzene, $C_6H_3(C_6H_5)_3$.

Diphenyl, $C_{12}H_{10}$ (*Fittig*, 1862). When bromo-benzene in ethereal solution is treated with sodium, a synthesis of diphenyl, analogous to the *Fittig* reaction (p. 357), is effected:

$$2C_6H_5Br + Na_2 = C_6H_5—C_6H_5 + 2NaBr.$$

Diphenyl also results when the vapour of benzene is led through a red-hot tube, this being the most convenient mode of preparing it. It is contained in coal tar. Large colourless

plates, readily soluble in alcohol and ether; M. Pt. 71°, B. Pt. 254°.

Chromic acid oxidizes diphenyl to benzoic acid, one of the two benzene nuclei being destroyed, thus leaving only one carbon atom joined to the other benzene residue. From this and from its synthesis, the constitutional formula of diphenyl follows as $C_6H_5—C_6H_5$.

Derivatives.

(See Summary; also *Schultz*, A. **207**, 311).

Like benzene, diphenyl is the mother substance of an extended series of derivatives.

Even the entrance of only one substituent produces isomers, since the latter may stand either in the *o*-, *m*-, or *p*-position to the point of junction of the two benzene residues. The same thing applies in still greater degree to isomeric di-derivatives, of which *o-o*-, *p-p*-, *o-p*- etc. compounds can exist. The constitution of these is elucidated either from their syntheses or from their products of oxidation; thus a chloro-diphenyl, $C_{12}H_9Cl$, which yields *p*-chloro-benzoic acid when oxidized by chromic acid, is obviously *p*-chloro-diphenyl.

The substituents take up the *p*-position for choice; in di-derivatives the *p-p*- (and to a lesser extent the *o-p*-) position.

Di-*p*-diamido diphenyl, *benzidine*, $C_{12}H_8(NH_2)_2 = \begin{matrix} C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{matrix}$ (*Zinin*, 1845), results from the reduction of di-*p*-dinitro-diphenyl (the direct nitration product of diphenyl); also, together with diphenyline, by the action of acids upon hydrazo-benzene, the latter undergoing a molecular transformation:

$$C_6H_5—NH—NH—C_6H_5 = NH_2—C_6H_4—C_6H_4—NH_2;$$

it is consequently formed directly from azo-benzene by treating it with tin and hydrochloric acid.

Benzidine is a diatomic base which crystallizes in colourless silky plates, readily soluble in hot water and alcohol and capable of sublimation; M. Pt. 122°. It is characterized by the sparing solubility of its sulphate, $C_{12}H_{10}(NH_2)_2.SO_4H_2$, and by various colour reactions. Like its homologues (tolidine,

etc.), it is of special importance in the colour industry, since, by coupling its diazo-compound (tetrazo-diphenyl chloride) with naphthol-sulphonic or naphthylamine-sulphonic acids, etc., colours are produced which dye unmordanted cotton directly, the so-called "substantive" or cotton dyes. To this class belongs the dye **Congo**, $\begin{array}{l} C_6H_4-N=N-C_{10}H_5(NH_2)(SO_3Na) \\ \vdots \\ C_6H_4-N=N-C_{10}H_5(NH_2)(SO_3Na) \end{array}$, prepared by means of naphthionic acid (p. 504), and the dye **Chrysamine G**, prepared with salicylic acid.

The isomeric **Diphenyline**, $\begin{array}{l} C_6H_4-\overset{(4)}{N}H_2 \\ |\,(1) \quad (2) \\ C_6H_4-NH_2 \end{array}$, results from *o*-*p*-dinitro-diphenyl, and also as a by-product in the preparation of benzidine from azo-benzene. Needles, M. Pt. 45°. Its sulphate is readily soluble.

Carbazole, $C_{12}H_9N$, $= \begin{array}{l} C_6H_4 \\ \vdots \\ C_6H_4 \end{array}\!\!>NH$, the imide of diphenyl, is contained in coal tar and in crude anthracene. It is formed *e.g.* by distilling *o*-amido-diphenyl over lime at a low red heat, or by passing the vapour of diphenylamine or of aniline through red-hot tubes, just as diphenyl is obtained from benzene: $(C_6H_5)_2NH = (C_6H_4)_2NH + H_2$.

It crystallizes in colourless plates sparingly soluble in cold alcohol, M. Pt. 238°. It distils unchanged and is characterized by its great capability of sublimation. Concentrated sulphuric acid dissolves it to a yellow solution, and it forms an acetyl- and a nitro-compound, etc. The nitrogen in it occupies the di-ortho-position; it thus appears, like indole, to be a pyrrol derivative, and it shows, in fact, most striking analogies to the latter (B. 21, 3299). It is convertible into:

p-**Diamido-carbazole**, $C_{12}H_7N(NH_2)_2$. For *constitution*, see B. 25, 128. The substantive dye **Carbazole yellow** is formed by the union of this compound with salicylic acid.

Benzidine-mono-, di-, etc. Sulphonic acids, *e.g.* $C_{12}H_6(NH_2)_2(SO_3H)_2$, are of technical importance in some cases, as are also **Benzidine-sulphone**, $C_{12}H_6(NH_2)_2(SO_2)$, and its **Sulphonic acids**, the sulphone resulting from the action of sulphuric acid upon benzidine.

The **Dioxy-diphenyls**, $C_{12}H_8(OH)_2$, of which four isomeric modifications are known, result partly by diazotizing benzidine, partly by fusing diphenyl-disulphonic acid with potash, and partly by fusing phenol with potash or by oxidizing it with permanganate; in the last case hydrogen is separated and two benzene residues join together.

Diphenylene oxide, $\begin{array}{l} C_6H_4 \\ \vdots \\ C_6H_4 \end{array}\!\!>O$, is obtained by distilling phenol with oxide

of lead; it crystallizes in plates which distil without decomposition (cf. *e.g.* B. 25, 2745).

Hexoxy-diphenyl, $C_{12}H_4(OH)_6$ (silvery glancing plates), which dissolves in potash with a beautiful violet-blue colour, is the mother substance of **Coerulignone** or **Cedriret**, $C_{16}H_{16}O_6$, a violet-coloured compound which is formed when crude pyroligneous acid is purified with chromate of potash, and also from the oxidation of the dimethyl-pyrogallol of beech-wood tar by means *e.g.* of potassic ferricyanide; in the latter case there is not only a joining together of the two benzene nuclei, but also a separation of hydrogen, with the production of a linking of somewhat the same nature as that in peroxides:

$$2C_6H_3{<}^{(O.CH_3)_2}_{(OH)} + O_2 = 2H_2O + \begin{array}{l} C_6H_2{<}^{(O.CH_3)_2}_{O>} \\ | \\ C_6H_2{<}^{O>}_{(O.CH_3)_2}. \end{array}$$

Coerulignone crystallizes in fine steel-grey needles soluble in concentrated sulphuric acid with a blue colour. Tin and hydrochloric acid convert it into **Hydro-coerulignone**, = tetramethyl-hexoxy-diphenyl, which is split up into methyl chloride and hexoxy-diphenyl on warming with concentrated hydrochloric acid (*Liebermann*).

The carboxylic acids of diphenyl are obtained (1) from the corresponding cyanides, which on their part are prepared by distilling the sulphonic acids of diphenyl with KCN, *e.g.* **Di-*p*-diphenyl-dicarboxylic acid**, $C_{12}H_8(CO_2H)_2$, a white powder insoluble in water, alcohol and ether; (2) by the oxidation of phenanthrene and similar compounds, *e.g.* **Diphenic acid**, $\begin{array}{l} C_6H_4.CO_2H \\ C_6H_4.CO_2H \end{array}$, a di-ortho-compound, crystallizing in needles or plates which are readily soluble in the solvents just mentioned; M. Pt. 229°. Both of these are dibasic acids, which yield diphenyl when heated with soda-lime.

The homologues of diphenyl are, like the latter, obtained by means of the *Fittig* reaction. Analogous to benzidine is *o*-**Tolidine**, $C_{12}H_6(CH_3)_2(NH_2)_2$, M. Pt. 128°, whose diazo-compound unites with naphthionic acid to the red substantive dye, **Benzo-purpurine 4 B**. Similarly **Di-anisidine** or **dimethoxy-benzidine**, $C_{12}H_6(O.CH_3)_2(NH_2)_2$, combines with *α*-naphthol-*α*-sulphonic acid (which see) to form a blue substantive dye, **Benzazurine G**.

Appendix. By the action of sodium upon a mixture of *p*-dibromo-benzene and bromo-benzene, there is formed **Diphenyl-benzene**, $C_6H_4(C_6H_5)_2$ (flat prisms, M. Pt. 205°), which is oxidizable to diphenyl-monocarboxylic and terephthalic acids.

When hydrochloric acid gas is led into acetophenone, $C_6H_5.CO.CH_3$, a reaction analogous to the formation of mesitylene from acetone ensues, and there is produced **Triphenyl-benzene**, $C_6H_3(C_6H_5)_3$ (1:3:5; rhombic plates).

XXVIII. DIPHENYL-METHANE GROUP.

Summary.

$(C_6H_5)_2{=}CH_2$ Diphenyl-methane. $(C_6H_5)_2{=}CH{-}CH_3$ Diphenyl-ethane.	$(C_6H_5)_2{=}CH.OH$ Benzhydrol.	$(C_6H_5)_2{=}CO$ Benzophenone.
$(C_6H_5)_2{=}CH{-}CO_2H$ Diphenyl-acetic acid.	$(C_6H_5)_2{=}C(OH){-}CO_2H$ Benzylic acid.	
$C_6H_5{-}CH_2{-}C_6H_4{-}CH_3$ Tolyl-phenyl-methanes.	$C_6H_5{-}CH(OH){-}C_6H_4{-}CH_3$ Tolyl-phenyl-carbinols.	$C_6H_5{-}CO{-}C_6H_4{-}C$[illegible] Tolyl-phenyl-keton[illegible]
$C_6H_5{-}CH_2{-}C_6H_4{-}CO_2H$ Benzyl-benzoic acids, etc.	$C_6H_5{-}CH(OH){-}C_6H_4{-}CO_2H$ Benzhydril-benzoic acids.	$C_6H_5{-}CO{-}C_6H_4{-}CO$[illegible] Benzoyl-benzoic aci[illegible]
$\begin{matrix}C_6H_4\\ \vert \\ C_6H_4\end{matrix}{>}CH_2$ Fluorene.	$\begin{matrix}C_6H_4\\ \vert \\ C_6H_4\end{matrix}{>}CH.OH$ Fluorenyl alcohol.	$\begin{matrix}C_6H_4\\ \vert \\ C_6H_4\end{matrix}{>}CO$ Diphenylene keton[illegible]

Diphenyl-methane is derived from methane by the substitution of two hydrogen atoms by two phenyl-groups, just as toluene is by the substitution of one. It consequently resembles the latter hydrocarbon in most of its relations, with this important difference that, as it no longer contains a CH_3-group, it cannot yield an acid containing an equal number of carbon atoms in the molecule upon oxidation; combination with oxygen produces benzhydrol and benzophenone. As soon, however, as more carbon atoms are made to enter the molecule, the same conditions repeat themselves as in the case of toluene, xylene, etc., and the most various acids, alcohol-acids, ketone-acids, etc. can be obtained from the resulting homologues.

***Formation* of diphenyl-methane and its derivatives.**

1. Diphenyl-methane is produced by the action of benzyl

chloride upon benzene, in presence of zinc dust (*Zincke*, A. 159, 374), or of aluminium chloride (*Friedel* and *Crafts*):

$$C_6H_5—CH_2Cl + C_6H_6 = C_6H_5—CH_2—C_6H_5 + HCl.$$

The homologues of benzene, and also the phenols and tertiary amines, *may be used here instead of benzene itself.*

In an exactly analogous manner diphenyl-methane results from the action of methylene chloride, CH_2Cl_2, upon benzene in presence of chloride of aluminium:

$$CH_2Cl_2 + 2C_6H_6 = CH_2(C_6H_5)_2 + 2HCl.$$

2. Diphenyl-methane hydrocarbons are formed by the action of the fatty aldehydes, *e.g.* acetic or formic aldehyde, upon benzene, etc. in the presence of concentrated sulphuric acid (*Baeyer*, B. 6, 221).

$$CH_3—CHO + 2C_6H_6 = \overbrace{CH_3—CH(C_6H_5)_2}^{\text{Diphenyl-ethane.}} + H_2O.$$

The acetic and formic aldehydes are employed here in the form of para-aldehyde and methylal. Formic aldehyde itself condenses with aniline to diamido-, and with dimethyl-aniline to tetramethyl-diamido-diphenyl-methane (which see). When aromatic aldehydes are used, triphenyl-methane derivatives result (p. 485).

2a. Aromatic alcohols react with benzene and sulphuric acid in an analogous manner (*V. Meyer*):

$$C_6H_5—CH_2.OH + C_6H_6 = C_6H_5—CH_2—C_6H_5 + H_2O.$$

Similar reactions have also been brought about by means of ketones, aldehyde-acids and ketone-acids on the one hand, and phenol and tertiary anilines on the other.

3. Benzophenone is produced by the action of benzoic acid upon benzene in presence of P_2O_5 (*Merz*, B. 6, 536):

$$C_6H_5—CO.OH + C_6H_6 = C_6H_5—CO—C_6H_5 + H_2O.$$

4. Benzophenone and the analogous ketones result upon heating the mixed calcium salts of the aromatic acids, according to the general mode of formation 2 of the ketones; thus calcium benzoate heated alone yields benzophenone:

$$C_6H_5.CO_2ca + C_6H_5.CO_2ca = C_6H_5.CO.C_6H_5 + CaCO_3.$$

Mixed ketones (p. 152) can be prepared in the same way.

5. Ketones are likewise produced by the action of benzoyl-chloride, $C_6H_5CO.Cl$, etc. upon benzene, etc. in presence of Al_2Cl_6 (*Friedel* and *Crafts*; also *Ador*, B. **10**, 1854):

$$C_6H_5.CO.Cl + C_6H_6 = C_6H_5.CO.C_6H_5 + HCl.$$

In this case also, as in method 3, phenols (or, better, phenolic ethers) or tertiary amines may be employed in place of the benzene hydrocarbons.

5ᵃ. Since the acid chlorides are formed from the benzenes with carbonyl chloride and zinc chloride, these reagents may be used directly for the production of ketones, under suitable conditions.

6. The above ketones are, like all others, converted into their corresponding hydrocarbons by distilling over zinc dust, or by heating with hydriodic acid and phosphorus, etc. (cf. p. 46).

1. **Diphenyl-methane**, $(C_6H_5)_2CH_2$, is most conveniently prepared from benzyl chloride, benzene and Al_2Cl_6. It crystallizes in colourless needles of very low melting point (26°), is readily soluble in alcohol and ether, has a pleasant odour of oranges, and distils unaltered; B. Pt. 262°.

It yields nitro-, amido-, and oxy-derivatives. ***p*-Diamido-diphenyl-methane**, $CH_2(C_6H_4NH_2)_2$, is obtained by heating anhydro-formaldehyde-aniline, $C_6H_5.N{=}CH_2$ (which see), with aniline and aniline salt. Lustrous silvery plates; M. Pt. 87°. It may be used for the preparation of fuchsine." By the action of bromine, aided by warming, **Diphenyl-bromo-methane**, $(C_6H_5)_2CHBr$, is obtained, and when this latter is heated with water to 150°, it passes into:

Benzhydrol, *diphenyl-carbinol*, $(C_6H_5)_2CH.OH$, which also results from benzophenone and sodium amalgam. It crystallizes in glancing silky needles, possesses in every respect the character of a secondary alcohol (forming compound ethers, amines, etc.), and is readily oxidizable to the corresponding ketone:

Benzophenone, *diphenyl-ketone*, $(C_6H_5)_2CO$. This compound is prepared by distilling benzoate of lime (*Péligot*, 1834), and also results directly from the oxidation of diphenyl-methane with chromic acid. It is the simplest pure aromatic ketone, and possesses the ketonic character in its entirety, being reducible to benzhydrol, yielding with PCl_5 a dichloride, $(C_6H_5)_2C{=}Cl_2$, and combining with phenyl-hydrazine, etc.

It is characterized by being dimorphous, crystallizing in large rhombic prisms, M. Pt. 49° (stable), and also in rhombohedra, M. Pt. 27° (unstable); B. Pt. 297°. Fused potash decomposes it into benzoic acid and benzene, while red-hot zinc dust regenerates diphenyl-methane.

Among its derivatives may be mentioned **Di-*p*-diamido-benzophenone**, $CO(C_6H_4.NH_2)_2$, which is obtained by boiling fuchsine with hydrochloric acid; M. Pt. 237°. The tetra-methyl compound, **Tetramethyl-diamido-**

benzophenone, $CO[C_6H_4N(CH_3)_2]_2$, **results from the action of** $COCl_2$ **upon** dimethyl-aniline:

$$COCl_2 + 2C_6H_5.N(CH_3)_2 = CO[C_6H_4N(CH_3)_2]_2 + 2HCl.$$

It is nearly related to certain dyes, being converted into methyl violet (p. 491) upon further treatment with dimethyl-aniline, and into **Auramine** or its derivatives (beautiful yellow dyes) by ammonia or amine bases respectively (B. **20**, 3260).

The *p*-position of the amido-groups has been proved.

p-**Dioxy-benzophenone,** $[C_6H_4(OH)_2]CO$, results among other methods from the decomposition of complicated benzene dyes, such as rosaniline and aurin, by heating these with water or with alkalies. It can be prepared synthetically from anisaldehyde (B. **14**, 328), and therefore contains the hydroxyls in the *p*-position; see also B. **24**, 1340. A derivative of *o*-dioxy-benzophenone is:

Diphenylene-ketone oxide, *Xanthone,* $C_6H_4<{CO \atop O}>C_6H_4$ (*Graebe,* A. **254**, 265), which is readily formed by abstracting the elements of water from phenyl-salicylic acid by strong sulphuric acid. Its dioxy-compound is

Euxanthone, $(HO)C_6H_3<{CO \atop O}>C_6H_3(OH)$, which is prepared from the yellow pigment Indian yellow or "Piuri," and which has also been synthetized. Bright yellow needles; M. Pt. 240°.

A **Trioxy-benzophenone** is obtained on warming an alcoholic solution of pyrogallol with benzene trichloride or benzoic acid. It is a yellowish dye, which is used with a mordant (in the same way as alizarin). B. **24**, 967, Ref. 378.

Homologues of Diphenyl-methane; Fluorene.

2. **Diphenyl-ethane,** $(C_6H_5)_2CH—CH_3$ (unsymmetrical, see p. 496), is obtained from benzene and para-aldehyde as given on p. 481. It is a liquid which boils without decomposition and which is oxidized to benzophenone by chromic acid. From it is derived:

Benzilic acid, *diphenyl-glycollic acid,* $(C_6H_5)_2—C(OH)—CO_2H$, which results by a molecular transformation upon fusing benzile (p. 497) with potash. It crystallizes in needles or prisms, soluble in H_2SO_4 with a blood-red colour, and is reduced by hydriodic acid to:

Diphenyl-acetic acid, $(C_6H_5)_2=CH—CO_2H$ (needles or plates), which on its part is obtained synthetically from phenyl-bromacetic acid, $C_6H_5—CHBr—CO_2H$, benzene and zinc dust, according to mode of formation 1, p. 480; this yields proof of its constitution. Both substances give benzophenone upon oxidation; here, therefore, as in the simpler cases, all the carbon is separated which is not directly linked to the benzene nuclei.

3. **Tolyl-phenyl-methanes,** $C_6H_5—CH_2—C_6H_4—CH_3$. **The** *p*- **and** *o*- **compounds are obtained from benzyl chloride and toluene, as given at**

p. 480. They yield on oxidation the corresponding **Tolyl-phenyl-ketones**, and finally the Benzoyl-benzoic acids (see below).

Tolyl-phenyl-ketones, C_6H_5—CO—C_6H_4—CH_3 (see summary, p. 480). For preparation, see above. Of the *p*-compound there exist two stereo-isomeric *p*-**Tolyl-phenyl-ketoximes**, the investigation of which has contributed materially towards the development of the theory of nitrogen-isomerism (see p. 158; also *Hantzsch*, B. **23**, 2325, 2776):—

$$\text{(I.)}\quad \begin{array}{c} CH_3{-}C_6H_4{-}C{-}C_6H_5 \\ \| \\ N{-}OH \end{array} \quad \text{and (II.)} \quad \begin{array}{c} C_6H_5{-}C{-}C_6H_4{-}CH_3 \\ \| \\ N{-}OH \end{array}$$

They yield structurally isomeric anilides by the *Beckmann* molecular transformation, the stable *anti*-tolyl-phenyl-ketoxime (formula I.) giving toluic anilide, CH_3—C_6H_4—CO—NHC_6H_5 (which is decomposable into toluic acid and aniline); while the unstable *syn*-tolyl-phenyl-ketoxime (formula II.) gives rise to benzo-toluidide, C_6H_5—CO—NH$C_6H_4CH_3$ (decomposable into benzoic acid and toluidine), together with toluic anilide, because the conditions of the reaction are such that it partly changes into the *anti*-modification. (*N.B.*—The *Beckmann* transformation, just alluded to, is brought about by treatment with a solution of hydrochloric acid gas in glacial acetic acid and acetic anhydride, or treatment in ethereal solution with phosphorus pentachloride, and then with water; cf. B. **20**, 2581; **24**, 52, 4028).

Benzoyl-benzoic acids, C_6H_5—CO—C_6H_4—CO_2H (B. **6**, 907). Of these the *o*-acid, for example (M. Pt. 127°), has also been prepared synthetically by heating phthalic anhydride with benzene and Al_2Cl_6. They are reducible to benzhydril-benzoic acids (or anhydrides) and benzyl-benzoic acids (see summary). When the *o*-acid is heated with P_2O_5 to 180°, it yields anthraquinone, various transformations into the anthracene series having been effected from *o*-tolyl-phenyl-methane and -ketone.

4. **Fluorene**, *diphenylene-methane*, $\begin{array}{l} C_6H_4 \\ \,\vert \\ C_6H_4 \end{array}\!\!>CH_2$, stands in the same relation to diphenyl-methane as carbazole (p. 478) does to diphenylamine; it is at the same time a diphenyl and a methane derivative. It is contained in coal tar, and is produced when diphenyl-methane is led through red-hot tubes (like diphenyl from benzene), and also by passing the vapour of diphenylene-ketone over red-hot zinc dust. It crystallizes in colourless plates with a violet fluorescence; M. Pt. 113°, B. Pt. 295°. The corresponding ketone, **Diphenylene-ketone**, $C_{12}H_8$=CO (yellow prisms, M. Pt. 84°), is obtained *e.g.* by heating phenanthrene-quinone with lime, and is converted into **Fluorenyl alcohol** (p. 480; colourless plates, M. Pt. 153°) by nascent hydrogen, and into diphenyl-carboxylic acid, C_6H_5—C_6H_4—CO_2H, by fusion with potash.

5. **Tolyl-phenyl-ethane**, $(C_6H_5)(C_7H_7)CH$—CH_3, results from the condensation of styrene with toluene (B. **24**, 2785). Styrene condenses with phenols in an analogous manner (B. **25**, 3889).

XXIX. TRIPHENYL-METHANE GROUP.

Triphenyl-methane, $CH(C_6H_5)_3$, results from the entrance of three phenyl groups into the methane molecule; among its homologues are *e.g.* Tolyl-diphenyl-methane, $CH<^{(C_6H_5)_2}_{C_6H_4.CH_3}$, Ditolyl-phenyl methane, $CH<^{(C_6H_5)}_{(C_6H_4.CH_3)_2}$, etc.

These hydrocarbons are of especial interest as being the mother substances of an extensive series of dyes.

Their *formation* is effected in a manner analogous to that of the diphenyl-methane derivatives, *i.e.* by the aid of zinc dust or aluminium chloride when chlorine compounds are used, or by the aid of phosphoric anhydride when oxygen compounds are employed.

Thus, triphenyl-methane results:

1. From benzal chloride and benzene:

$$C_6H_5.CHCl_2 + 2C_6H_6 = CH(C_6H_5)_3 + 2HCl;$$

1a. from benzaldehyde, benzene and zinc chloride (see p. 481);

2. from chloroform and benzene by means of Al_2Cl_6:

$$3C_6H_6 + CHCl_3 = CH(C_6H_5)_3 + 3HCl;$$

3. from benzhydrol and benzene:

$$(C_6H_5)_2=CH.OH + C_6H_6 = (C_6H_5)_2=CH.(C_6H_5) + H_2O.$$

The leuco-base of bitter-almond-oil green (cf. p. 488) results from benzaldehyde and dimethyl-aniline:

$$C_6H_5.CHO + 2C_6H_5.N(CH_3)_2 = C_6H_5.CH=[C_6H_4.N(CH_3)_2]_2 + H_2O.$$

By using other amine bases and also phenols, a series of allied compounds (which are often dyes) is obtained, the separation of water being facilitated by the addition of zinc chloride, concentrated sulphuric acid, or anhydrous oxalic acid.

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1. Triphenyl-methane, $C_{19}H_{16}$, = $CH(C_6H_5)_3$ (*Kekulé* and *Franchimont*, B. 5, 906). This compound may be prepared from chloroform and benzene by the *Friedel-Crafts* reaction (cf. A. 194, 152), diphenyl-methane being produced at the same time; also by diazotizing *p*-leucaniline, $C_{19}H_{13}(NH_2)_3$, *i.e.* by eliminating the amido-groups from it. It crystallizes in beautiful white prisms, insoluble in water and only slightly

soluble in cold alcohol, but readily soluble in hot alcohol, ether and benzene; M. Pt. 93°, B. Pt. 359°.

It crystallizes from benzene with one molecule of "benzene of crystallization," which is also the case with many triphenyl-methane derivatives. When triphenyl-methane is treated with bromine in a solution of carbon bisulphide, the methane hydrogen atom is exchanged for bromine with the formation of :

Triphenyl-methane bromide, $(C_6H_5)_3.CBr$, which, when boiled with water, goes into :

Triphenyl-carbinol, $(C_6H_5)_3C.(OH)$. This crystallizes in glancing prisms, M. Pt. 159°, and can be sublimed unchanged; it may also be prepared directly by oxidizing a solution of triphenyl-methane in glacial acetic acid with chromic acid.

Fuming nitric acid acts upon triphenyl-methane to form **Trinitro-triphenyl-methane**, $(C_6H_4.NO_2)_3.CH$ (yellow scales), which is in its turn converted into :

Trinitro-triphenyl-carbinol, $(C_6H_4.NO_2)_3C(OH)$, by chromic acid. The latter gives para-rosaniline, $(C_6H_4.NH_2)_3C.OH$, when treated with zinc dust and glacial acetic acid, and the former, para-leucaniline (p. 489).

Homologous with triphenyl-methane are the :

2. **Tolyl-diphenyl-methanes**, $(C_6H_5)_2{=}CH{-}C_6H_4(CH_3)$. From these also dyes are derived, especially from *m*-**Tolyl-diphenyl-methane** (in which the CH_3 occupies the meta-position with regard to the methane carbon atom), which can be prepared by diazotizing ordinary leucaniline; it crystallizes in small prisms, M. Pt. 59·5°.

Triphenyl-methane Dyes.

Of the derivatives of triphenyl-methane and of tolyl-diphenyl-methane, those are especially interesting which result from them by the entrance of amidogen or hydroxyl (or also carboxyl). The entrance of three amido- or hydroxyl-groups converts them into the leuco-compounds of dyes, some of which latter are of great value. Two amido-groups suffice for the full development of the dye character only when the amido-hydrogen atoms are replaced by alcoholic radicles, one amido-group being insufficient for this (see under m-amido-triphenyl-methane).

We distinguish between the following groups:

1. that of diamido-triphenyl-methane (the bitter-almond-oil green group);

2. that of triamido-triphenyl-methane (the rosaniline group);

3. that of trioxy-triphenyl-methane (the aurin group);

4. that of triphenyl-methane-carboxylic acid (the eosin group).

Leuco-bases or **Leuco-compounds** of dyes are compounds which result from the reduction of the dyes themselves (in most cases by the addition of two atoms of hydrogen); they are colourless, but are converted into the dyes by oxidation.

All the dyes of the triphenyl-methane group, and also indigo, methylene blue, safranine, etc. are capable of yielding such leuco-compounds (mostly by the action of zinc and hydrochloric acid, stannous chloride, or ammonium sulphide).

The oxidation of the leuco-compounds is often quickly effected by the oxygen of the air (*e.g.* in the cases of indigo white and of leuco-methylene blue); in the triphenyl-methane group it is slower and frequently more complicated. Leuco-bitter-almond-oil green readily goes into the corresponding colour-base when treated with PbO_2 in acid solution, and leucaniline does the same when warmed with chloranil in alcoholic solution, or when its hydrochloride is heated either alone or with a concentrated solution of arsenic acid, or with metallic hydroxides such as $Fe_2(OH)_6$.

1. Amido- and Diamido-triphenyl-methane Group.

p-**Amido-triphenyl-methane** can be synthetized either by the condensation of *p*-nitro-benzaldehyde with benzene and subsequent reduction, or from benzhydrol and aniline. Large prisms; M. Pt. 84°. The corresponding carbinol is colourless and its salts red; these do not dye animal fibres.

p-**Diamido-triphenyl-methane,** $C_6H_5—CH(C_6H_4.NH_2)_2$, is prepared by the action of zinc chloride or of fuming hydrochloric acid upon a mixture of benzaldehyde and aniline sulphate or chloride:

$$C_6H_5.CHO + 2C_6H_5NH_2 = C_6H_5.CH{=}(C_6H_4.NH_2)_2 + H_2O.$$

It crystallizes in glancing prisms. The colourless salts yield an unstable blue-violet dye, Benzal violet, upon oxidation. Methylation converts the base into:

Tetramethyl-di-*p*-amido-triphenyl-methane, *leuco-malachite green*, $C_6H_5—CH{=}[C_6H_4.N(CH_3)_2]_2$, which is prepared on the technical scale by

heating benzaldehyde and dimethyl-aniline with zinc chloride or anhydrous oxalic acid (p. 485, *O. Fischer*, A. **206**, 103). It forms colourless plates or prisms. As a diatomic base it yields colourless salts, and is slowly converted by the air, but immediately by other oxidizing agents, such as $PbO_2 + H_2SO_4$ into (the salts of):

Tetramethyl-diamido-triphenyl-carbinol, $C_6H_5.C(OH)—[C_6H_4N(CH_3)_2]_2$. The free base is obtained by precipitating the salts with alkali. It crystallizes in colourless needles and dissolves in cold acid to a colourless solution; upon warming, however, the intense green colouration of the salts is produced. (For an explanation of this, see p. 490.)

The double salt with zinc chloride or the oxalate of this base is the valuable dye **Bitter-almond-oil green,** *malachite green* or *Victoria green*, which forms green plates, readily soluble in water. This can also be prepared directly by heating benzotrichloride with dimethyl-aniline and chloride of zinc (*Doebner*). **Brilliant green** is the corresponding ethyl compound.

Diethyl-dibenzyl, etc., compounds are also known, the sulphonic salts of which are valuable dyes, *e.g.* **Acid green**, etc.

If, instead of benzaldehyde, *o*-, *m*-, or *p*-nitro-benzaldehyde is used, nitro-derivatives of (leuco-) malachite green are obtained.

The analogous *p*-**Nitro-diamido-triphenyl-methane,** $C_6H_4(NO_2)—CH(C_6H_4.NH_2)_2$, can be prepared from *p*-nitro-benzaldehyde, aniline sulphate and sulphuric acid. It goes into para-leucaniline upon reduction. The reduction of the isomeric *m*- and *o*-compounds yields isomers of leucaniline (Pseudo- and Ortho-leucanilines), which give violet and brown dyes upon oxidation.

2. Rosaniline Group.

Fuchsine or magenta was first obtained in 1856 by *Natanson* [who noticed the formation of a red substance, in addition to that of aniline hydrochloride and ethylene-aniline, when ethylene chloride was allowed to act upon aniline at a temperature of 200° (A. **98**, 297)], and shortly afterwards by *A. W. Hofmann* (by the action of carbon tetrachloride upon aniline), and was first prepared on the technical scale in 1859. *Hofmann's* scientific researches on this subject date from 1861. The chemical constitution was made clear by *Emil* and *Otto Fischer* in 1878 (A. **194**, 242). (Cf. also *Caro* and *Græbe*, B. **11**, 1116.)

The rosaniline dyes are derived partly from triphenyl-methane and partly from *m*-tolyl-diphenyl-methane; in the former case they are often designated para-compounds (*e.g.*

"para-rosaniline," because it is prepared from aniline and para-toluidine; "para-rosolic acid").

Para-leucaniline, $C_{19}H_{19}N_3$, and **Leucaniline,** $C_{20}H_{21}N_3$, result from the reduction of the corresponding trinitro-compounds and also of the corresponding dye-bases, para-rosaniline and rosaniline; the first named likewise from the reduction of *p* nitro-diamido-triphenyl methane. The free leuco-bases are thrown down by ammonia from solutions of their salts as white or reddish flocculent precipitates, and crystallize in colourless needles or plates; they melt at 203° and 100° respectively. As triatomic bases they form colourless crystalline salts.

Para-rosaniline, $C_{19}H_{19}N_3O$, and **Rosaniline,** $C_{20}H_{21}N_3O$, are the bases of the fuchsine dyes. They are obtained by precipitating solutions of their salts with alkalies, and crystallize from hot water or alcohol in colourless needles or plates, which become red in the air. Both are triatomic bases, stronger than ammonia.

They yield tri-diazo-compounds with nitrous acid, compounds which go into the corresponding phenol dyes (aurin and rosolic acid) when boiled with water; they are therefore primary.

Constitution. The relations between the rosanilines and triphenyl-methane have been made clear by the transformation of leucaniline (by diazotizing it) into tolyl-diphenyl-methane, and the analogous conversion of para-leucaniline into triphenyl-methane (*E.* and *O. Fischer*, loc. cit.).

Para-leucaniline is thus triamido-triphenyl-methane, while leucaniline is triamido-tolyl-diphenyl-methane. The dye-bases belonging to them are the corresponding carbinols, *e.g.* rosaniline is triamido-tolyl-diphenyl-carbinol. The three amido-groups can be introduced synthetically, as given above. They are distributed equally among the three benzene nuclei, as is clear from the synthesis of para-leucaniline by means of *p*-nitro-benzaldehyde (p. 488). We have, therefore, *e.g.* the following formulae:

$$CH\begin{cases}C_6H_4.NH_2\\ C_6H_4.NH_2\\ C_6H_4.NH_2\end{cases} \qquad\qquad C(OH)\begin{cases}C_6H_4.NH_2\\ C_6H_4.NH_2\\ C_6H_3(CH_3).NH_2.\end{cases}$$

Para-leucaniline. Rosaniline.

The para-position of the NH_2-groups with regard to the methane carbon atom is proved as follows: (1) Para-rosaniline yields *p*-dioxy-benzophenone (p. 483; B. 11, 1434) when heated with water, while rosaniline gives *p*-diamido-methyl-benzophenone (B. 16. 1928; 19.

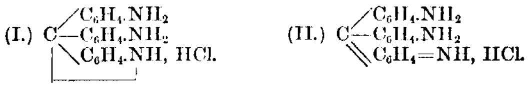
107). (2) Diamido-triphenyl-methane (from benzaldehyde and aniline) is a di-*p*-compound, because it is likewise convertible into di-*p*-oxy-benzophenone (B. **12**, 1466). Para-leucaniline (from *p*-nitro-benzaldehyde and aniline, B. **15**, 100) is therefore a tri-*p*-compound.

The salts of rosaniline and para-rosaniline, **Fuchsine**, $C_{20}H_{20}N_3Cl$, **Rosaniline nitrate**, $C_{20}H_{20}N_3(NO_3)$. **Rosaniline acetate**, $C_{20}H_{20}N_3(C_2H_3O_2)$, etc. are the actual dyes. While they possess a magnificent fuchsine-red colour in solution, and have intense colouring power (dyeing wool and silk without a mordant), their crystals are of a brilliant metallic green with cantharides glance, *i.e.* of nearly the complementary colour. They are fairly soluble in hot water and alcohol.

In the formation of the salts water is separated, thus:—

$$C(OH)(C_6H_4.NH_2)_3 + HCl = C_{19}H_{17}N_3,\ HCl + H_2O.$$

In the dyes there is therefore present a peculiar nitrogen-carbon linking (see formula I.), which is reminiscent of the older quinone formula ("quinoid linking"); but the simpler constitution (formula II.), which corresponds to the newer quinone formula, is equally justifiable:—



Para-rosaniline hydrochloride.

An analogous separation of water is also observed in the formation of salts of the malachite green base, but this only takes place upon warming, as is proved by the fact that it dissolves without colour in cold acids, and that the intense colouration of the salts first becomes apparent after warming the solution.

In addition to the above salts there also exist acid ones, *e.g.* $C_{20}H_{20}N_3Cl + 3HCl$ (which yields a yellow-brown solution, not a fuchsine-coloured one); these dissociate into the neutral salts and free acid upon the addition of much water.

Some chemists regard the rosaniline salts, etc., as *carbinol esters, e.g.* para-rosaniline hydrochloride as $(NH_2.C_6H_4)_3C.Cl$ (*Rosenstiehl; V. v. Richter*).

In the manufacture of magenta, either a mixture of aniline with *o*- and *p*-toluidine is oxidized by syrupy arsenic acid, or a mixture of nitro-benzene with aniline and toluidine is heated with iron filings and hydrochloric acid (*Coupier*). Nitro-toluene may also be employed instead of nitro-benzene.

Instead of arsenic acid, stannic chloride or mercuric chloride or nitrate, etc., may be used for the oxidation. If *o*-toluidine is present in the mixture to be oxidized, rosaniline is formed, and if it is absent,

para-rosaniline. When pure aniline is oxidized alone, it yields no fuchsine at all, but products of the nature of indulin. This is explained by the fact that for the formation of fuchsine a carbon atom is required which shall serve to link the benzene nuclei together, a so-called "methane-carbon"; in the action of carbon tetrachloride upon aniline, this carbon originates from the tetrachloride, and in the oxidation of a mixture of aniline and toluidine, from the methyl group of the latter, as is shown in the following equation:

$$H_3C\text{—}C_6H_4.NH_2 + C_6H_5.NH_2 + C_6H_5.NH_2 - 3H_2 = C\begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH \end{cases}$$

Para-rosaniline and rosaniline also result upon heating *p*-diamido-diphenyl-methane (p. 482) with aniline and *o*-toluidine respectively, in presence of an oxidizing agent (B. **25**, 302).

When rosaniline is heated with hydrochloric or hydriodic acid to 200°, it is split up into aniline and toluidine; when superheated with water, para-rosaniline yields *p*-dioxy-benzophenone, ammonia, and phenol. When boiled with hydrochloric acid, rosaniline breaks up into *p*-diamido-benzophenone and *o*-toluidine (B. **16**, 1928; **19**, 107; **22**, 988). A solution of fuchsine is decolourized by sulphurous acid, an addition-product, fuchsine-sulphurous acid, being formed. This solution is a delicate reagent for aldehydes, which colour it violet-red (see p. 146; B. **21**, Ref. 149, etc.).

For the *homologues* and *isomers* of rosaniline, see p. 489; B. **15**, 1543; **24**, 553.

Acid Magenta, or **Fuchsine S**, is a sulphonic acid of fuchsine and a valuable *acid dye* (in a faintly acid solution it adheres to wool and silk).

Derivatives of Rosaniline.

1. Methylated rosanilines (*Hofmann*, *Lauth*).

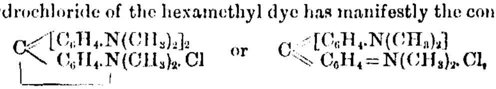
The red colour of para-rosaniline and of rosaniline is changed into violet by the entrance of methyl or ethyl, the intensity of the latter colour increasing with an increasing number of these groups. The salts of **Hexamethyl-para-rosaniline** have a magnificent bluish-violet shade. In the manufacture of these "**Methyl-violets**" one may either (1) methylate rosaniline (by means of CH_3Cl or CH_3I); or (2) oxidize, instead of aniline, a methylated aniline such as dimethyl-aniline (*e.g.* by means of cupric salts), whereby para-rosaniline derivatives result; or, (3) allow phosgene to act upon dimethyl-aniline (or

the latter to act upon the tetramethyl-diamido-benzophenone at first produced) (cf. B. 17, Ref. 339):

$$COCl_2 + 3C_6H_5.N(CH_3)_2 = C(OH)[C_6H_4.N(CH_3)_2]_3 + 2HCl.$$

In the last case hexamethyl-violet, termed "**Crystal violet**" on account of the beauty of its crystals, results, while the methyl-violets prepared by methods (1) and (2) are mixtures of hexa-, penta-, and tetra-methyl-rosanilines and are amorphous.

The hydrochloride of the hexamethyl dye has manifestly the constitution:



the H-atom of the combined HCl breaking off with the hydroxyl of the compound as water.

Hexamethyl-carbinol no longer contains an amido-hydrogen atom, in consequence of which any further methyl chloride or iodide cannot effect an exchange of hydrogen for alkyl but can only form an addition-compound. Such addition causes a change of colour from violet to green; thus the compound $C_{19}H_{12}(CH_3)_6N_3Cl$, CH_3Cl is the dye **Methyl green** or *Light green*.

The hexa-substituted rosanilines, which contain benzyl as well as methyl or ethyl groups, are similar to crystal violet; their sulphonic acids form useful dyes, *e.g.* **Acid violet**.

2. **Phenylated rosanilines.** By the successive entrance of phenyl groups into rosaniline, there result in the first instance violet dyes, which change to blue when three phenyl groups have entered. **Triphenyl-rosaniline-hydrochloride** or "aniline blue" is a beautiful blue dye, insoluble in water but soluble in alcohol. It is prepared by heating rosaniline with aniline in presence of benzoic acid, when ammonia is eliminated; or by the oxidation of aniline already phenylated, *i.e.* diphenylamine, *e.g.* by means of oxalic acid. The latter supplies the methane carbon atom, and the beautiful "diphenylamine blue" or **Sprit blue** which results is a para-rosaniline derivative. Formic aldehyde can also supply the methane carbon atom.

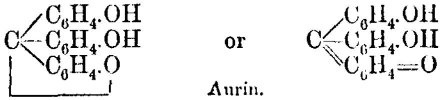
Victoria blue results from the condensation of tetramethyl-diamido-benzophenone with phenyl-α-naphthylamine.

The dyes which are insoluble in water are rendered soluble by sulphurating them, in which condition they form the **Nicholson's blue, Water blue,** and **Light blue,** etc., of commerce.

3. Trioxy-triphenyl-methane, $CH(C_6H_4.OH)_3$ (the Aurin group).

Rosolic acid was first observed by *Runge* in 1834.

The oxygenated analogues of para-rosaniline and rosaniline are **Aurin**, $C_{19}H_{14}O_3$, and **Rosolic acid**, $C_{20}H_{16}O_3$:



Aurin.

These likewise possess the dye-character, but, instead of being basic, they are acid dyes (phenol dyes); they are of far less value than the nitrogenous dyes which have been already described.

They are formed when the diazo-compounds of para-rosaniline or rosaniline are boiled with water (*Caro* and *Wanklyn*, 1866):

$$C(OH)(C_6H_4-N=N-SO_4H)_3 + 3H_2O = C(OH)(C_6H_4.OH)_3 + 3N_2 + 3H_2SO_4;$$
$$C(OH)(C_6H_4.OH)_3 = C(C_6H_4.OH)_2(C_6H_4.O) + H_2O.$$

(The carbinol which must be produced here in the first instance is incapable of existence, and gives up H_2O.) The constitutional formulæ just given follow from this close relation to the rosanilines.

Aurin is also obtained on heating phenol-sodium with carbon tetrachloride to 123°, and by heating phenol with oxalic and sulphuric acids to 130°–150° (*Kolbe* and *Schmitt*, 1859), the oxalic acid yielding the methane-carbon; rosolic acid results in an analogous manner from a mixture of phenol and cresol with arsenic and sulphuric acids. Phenol by itself yields no rosolic acid upon oxidation.

Aurin and rosolic acid crystallize in beautiful green needles or prisms with a metallic glance, dissolve in alkalies with a fuchsine-red colour, and are thrown down again from this solution by acids. The alkaline salts are decidedly unstable, aurin being but a weak phenol; at the same time it possesses a slightly basic character. An ammonium salt is known, which crystallizes in dark red needles with a blue shimmer. Upon reduction there are formed the leuco-compounds **Leucaurin**, $CH(C_6H_4.OH)_3$, and **Leuco-rosolic acid**, $CH(C_6H_4.OH)_2(C_6H_3[CH_3].OH)$, both of which crystallize in colourless needles of phenolic character. Superheating with water converts aurin into *p*-dioxy-benzophenone, $CO(C_6H_4.OH)_2$, and phenol; superheating with ammonia, into para-rosaniline.

Pittacall or *eupittone*, which is present in beech-wood tar, is a hexa-methoxylated aurin, $C_{19}H_8(OCH_3)_6O_3$.

4. Triphenyl-methane-carboxylic acid (the Eosin group).

(Cf. *Baeyer*, A. **183**, 1; **202**, 36).

Triphenyl-methane-carboxylic acid, $CH(C_6H_5)_2(C_6H_4.CO_2H)$, results from the reduction of phthalophenone (see below), and yields triphenyl-methane by the separation of CO_2. It crystallizes in colourless needles, M. Pt. 162°.

Triphenyl-carbinol-o-carboxylic acid, $C(OH)(C_6H_5)_2(C_6H_4.CO_2H)$. The anhydride of this acid, which is termed **Phthalophenone,** is obtained by heating phthalic chloride with benzene and Al_2Cl_6 (A. **202**, 50), and forms plates, M. Pt. 115°. The acid itself is incapable of existence, but its salts are got by dissolving the anhydride in alkalies. Phthalophenone is on the one hand a triphenyl-methane derivative and on the other a derivative of phthalic acid, in accordance with the constitutional formula:

$$C_6H_4<\begin{matrix}C(C_6H_5)_2\\CO\end{matrix}>O, \quad = \quad C<\begin{matrix}(C_6H_5)_2\\C_6H_4-CO\end{matrix};\ \text{(C—O ring)}$$

it is to be looked upon as diphenyl-phthalide (see phthalide, p. 460).

Phthalophenone is the mother substance of a large series of dyes, which are derived from it by the entrance either of hydroxyl or of amidogen. They are prepared by the action of phenols upon phthalic anhydride and are termed *Phthaleïns.* Phenol and resorcin, for example, yield the compounds:

$$C_6H_4<\begin{matrix}C(C_6H_4.OH)_2\\CO\end{matrix}>O \quad \text{and} \quad C_6H_4<\begin{matrix}C\left(\begin{matrix}C_6H_3(OH)\\C_6H_3(OH)\end{matrix}>O\right)\\CO\end{matrix}>O;$$

Phenol-phthaleïn. Fluoresceïn.

in the latter case a molecule of water is split off from two hydroxyls of the two resorcin residues. Phthaleïns of this kind (being oxy-phthalophenones) are converted by reduction into the oxy-derivatives of triphenyl-methane-carboxylic acid, which are termed "*Phthalines;*" *e.g.* phenol-phthaleïn into dioxy-triphenyl-methane-carboxylic acid (*i.e.* phenol-phthaline), $CH<\begin{matrix}(C_6H_4.OH)_2\\C_6H_4-CO_2H\end{matrix}$. The phthalines are colourless, and are to be looked upon as leuco-compounds of the phthaleïns. The phthaleïns include among themselves many dyes which are of technical value, *e.g.* the eosins (*Caro, Baeyer*, 1871).

For *constitution*, cf. also *Bernthsen*, Chem. Zeitung for 1892, p. 1956.

Phenol-phthaleïn, $C_{20}H_{14}O_4$, is prepared by heating phthalic anhydride with phenol and sulphuric acid or, better, stannic chloride (or oxalic acid) to 115–120°. It also results upon nitrating diphenyl-phthalide, reducing the two substituting nitro-groups to amido-ones, and transforming these into hydroxyl by diazotizing (A. **202**, 68). It crystallizes from alcohol in colourless crusts; in water it is nearly insoluble, but it dissolves in alkalies with a beautiful red colour which vanishes again on the addition of acids; it is thus a valuable indicator (B. **17**, 1017, 1097). It yields a **Di-acetyl** derivative and is reduced by potash and zinc dust to:

Phenol-phthaline (colourless needles), which dissolves in alkali to a colourless solution, but is readily reoxidized in this solution to phthaleïn.

Fluorane, $C_{20}H_{12}O_3$, which was formerly looked upon as being phenol-phthaleïn anhydride, results as by-product in the phenol-phthaleïn melt, and is the mother substance of fluoresceïn. For *constitution*, see B. **25**, 1385, 2118.

Fluoresceïn or *resorcin-phthaleïn*, $C_{20}H_{12}O_5 + H_2O$, is prepared by heating phthalic anhydride and resorcin to 200°. It forms a dark red crystalline powder, and dissolves in alcohol with a yellow-red colour, and in alkalies with a red colour and splendid green fluorescence. It is reducible to the phthaline "Fluorescin," and yields with bromine red crystals of tetrabromo-fluoresceïn, whose potassium salt, $C_{20}H_6Br_4O_5K_2$, is the magnificent dye **Eosin**. Fluorescing dyes are likewise formed in an analogous manner from all the derivatives of 1:3-dioxy-benzene, in which position 5 is unoccupied.

Instead of phthalic acid itself, chlorinated or brominated, etc., phthalic acids may be employed, so that, by gradually increasing the amount of halogen present, a whole series of yellow-red to violet-red eosins can be prepared, *e.g.* tetrabromo-di-iodo-eosin; these are known under the names of Erythrosin, Rose de Bengale, Phloxin, etc. It is worthy of note here that many other dibasic acids (*e.g.* succinic) and also benzoic acid are capable of yielding fluorescing compounds.

If the two hydroxyls of the resorcin residue in fluoresceïn are replaced by group $N(C_2H_5)_2$, **(Tetra-ethyl-) Rhodamin**, $C_{20}H_{12}O_3[N(C_2H_5)_2]_2$, results. This is a splendidly fluorescing red basic dye. It is produced by heating phthalic anhydride with diethyl-*m*-amido-phenol (p. 421; cf. also Formo-rhodamin).

Galleïn, $C_{20}H_{10}O_7$, is obtained in an analogous manner from pyrogallol and phthalic anhydride; it dissolves in alkalies with a blue colour. Galleïn contains two atoms of hydrogen less than the normal phthaleïn of pyrogallol; as in the case of coerulignone, two "peroxide" oxygen atoms are assumed here.

Its phthaline, Gallin, $C_{20}H_{14}O_7$, is transformed by concentrated

sulphuric acid into the "phthalidine" **Coerulin**, $C_{20}H_{12}O_6$, which yields the "phthalideïn" **Coeruleïn**, $C_{20}H_8O_6$, a valuable olive-green dye, upon oxidation. The mother substance of both the latter compounds is phenyl-anthranol (p. 511). For details, see A. **209**, 249.

XXX. DIBENZYL GROUP.

The modes of formation, etc. of the members of the dibenzyl group show that the two benzene nuclei in them are connected together by two carbon atoms; all of them are transformed into benzoic acid upon oxidation.

Summary.

$C_6H_5—CH_2—CH_2—C_6H_5$ Dibenzyl.	$C_6H_5—CH{=}CH—C_6H_5$ Stilbene.	$C_6H_5—C{\equiv}C—C_6H_5$ Tolane.

$C_6H_5—CH_2—CO—C_6H_5$ Desoxy-benzoïn.	$C_6H_5—CH(OH)—CH(OH)—C_6H_5$ Hydrobenzoïn.
$C_6H_5—CH(OH)—CO—C_6H_5$ Benzoïn.	$C_6H_5—CO—CO—C_6H_5$ Benzile.

Dibenzyl may be designated as symmetrical diphenyl-ethane (for the unsymmetrical compound, see p. 483), stilbene as *s*-diphenyl-ethylene, and tolane as diphenyl-acetylene.

Dibenzyl, $C_{14}H_{14}$. When benzyl chloride (2 mols.) is treated with sodium, the two liberated residues $C_6H_5—CH_2—$ (benzyl) join together with the formation of dibenzyl, a hydrocarbon which is isomeric with ditolyl and with tolyl-phenyl-methane. It crystallizes in needles or small plates, M. Pt. 52°, and sublimes unchanged.

Stilbene, *diphenyl-ethylene*, $C_{14}H_{12}$, forms monoclinic plates or prisms, M. Pt. 125°, which also boil without decomposition. It may be prepared *e.g.* by the action of sodium upon benzal chloride or oil of bitter almonds, or by passing the vapour of toluene or dibenzyl over heated oxide of lead, and possesses the full character of an olefine, giving—for instance—a dibromide, $C_6H_5—CHBr—CHBr—C_6H_5$, with bromine, and being converted into dibenzyl by hydriodic acid. ***p*-Diamido-stilbene**, $C_{14}H_{10}(NH_2)_2$, and its disulphonic acid (obtained by reducing *p*-nitro-toluene or its sulphonic acid in alkaline solution) are, like benzidine, mother substances of

"cotton dyes" (see p. 478). Just as ethylene bromide yields acetylene when boiled with alcoholic potash, so does stilbene dibromide yield:

Tolane, $C_{14}H_{10}$, which crystallizes in prisms or plates, M. Pt. 60°. Tolane corresponds with acetylene in its properties in so far that it combines with chlorine to a dichloride and a tetrachloride, and so on, but it does not yield metallic compounds since it contains no "acetylene hydrogen."

When stilbene dibromide is treated with silver acetate, two di-acetic esters are formed; and when these are saponified by alcoholic ammonia, two isomeric substances of the composition: $C_{14}H_{14}O_2$, $C_6H_5—CH(OH)—CH(OH)—C_6H_5$, **Hydro-benzoïn** and **Iso-hydrobenzoïn** or *s-diphenyl-glycol*, are produced. These likewise result from the action of sodium amalgam upon oil of bitter almonds. The former crystallizes in rhombic plates, M. Pt. 138°, and the latter in four-sided prisms, M. Pt. 119°, which are the more soluble of the two. These two compounds are stereo-isomeric, as are also their diacetyl esters (A. **198**, 115, 191).

The compounds **Benzoïn**, **Benzile** and **Desoxy-benzoïn,** which have already been referred to in the summary, are closely related to one another as their formulæ show, and can also be prepared from bitter almond oil. The latter "condenses" (p. 144) in alcoholic solution, under the influence of potassium cyanide, to benzoïn ($2C_7H_6O, = C_{14}H_{12}O_2$), which forms beautiful glancing prisms; nascent hydrogen reduces it to hydro-benzoïn, from which it also results upon oxidation. It reduces *Fehling's* solution even at the ordinary temperature, with the formation of benzile.

Benzile, $C_6H_5—CO—CO—C_6H_5$, is obtained by oxidizing benzoïn by means of nitric acid. It crystallizes in large six-sided prisms, M. Pt. 95°. It is oxidized to benzoic acid by CrO_3, and reduced by nascent hydrogen—according to the conditions—either to benzoïn or to desoxy-benzoïn. It reacts with hydroxylamine to produce:—

Benzile-monoxime, $C_6H_5—CO—C(N.OH)—C_6H_5$, and **Benzile-dioxime,** $(C_6H_5)_2=[C(N.OH)]_2$, both of which exist in stereo-isomeric modifications. Cf. *Auwers*, *V. Meyer*, B. **21**, 3510; **22**, 705, 1996; **23**, 3589; **24**, 3267; *Hantzsch* and *Werner*, B. **23**, 1, 3589; **24**, 3267.

Desoxy-benzoïn. The latter forms large plates, M. Pt. 55°, and may be sublimed or distilled unchanged. It can be prepared by the action of benzene and aluminic chloride upon the chloride of phenyl-acetic acid ($C_6H_5—CH_2—CO.Cl$), which is a proof of its constitution, and yields di-benzyl with hydriodic acid. Desoxy-benzoïn can also be prepared from benzile and benzoïn (B. **25**, 1728). One of its methylene hydrogen atoms is readily placeable by alkyl, just as in aceto-acetic ester. The residue, $C_6H_5—CH—CO—C_6H_5$, is termed "Desyle."

Benzilic acid, $(C_6H_5)_2=C(OH)—CO_2H$ (p. 483), results upon heating benzile with alcoholic potash, by a peculiar molecular transformation similar to that by which pinacoline is formed (p. 157).

A series of compounds homologous with di-benzyl, stilbene, etc., is also known. Carboxyl groups can likewise substitute in di-benzyl and stilbene, with the formation of phenyl-cinnamic acid, diphenyl-succinic acid, stilbene-dicarboxylic acid, etc.

Appendix.

Further, two or more benzene nuclei may be connected together through more than two carbon atoms. In indigo, for example, the two benzene residues are linked together by four carbon atoms, and the same holds good for the hydrocarbon which is its basis, viz., **Diphenyl-diacetylene**, $C_6H_5—C{\equiv}C—C{\equiv}C—C_6H_5$ (*Baeyer*). This last compound results from the oxidation of copper phenyl-acetylene, $C_6H_5—C{\equiv}C—Cu$, with a solution of potassium ferricyanide, crystallizes in long needles which melt at 88°, and combines with eight atoms of bromine to an octo-bromide. Its *o*-**Dinitro-derivative**, which is prepared in an analogous manner from *o*-nitro-phenyl-acetylene, yields indigo when treated first with sulphuric acid and then with sulphide of ammonium (see p. 470; also B. **16**, 53).

In **Dibenzoyl-acetic acid**, $(C_6H_5.CO)_2{=}CH—CO_2H$, a di-ketonic acid, whose ether is obtained by treating benzoyl-acetic ether with benzoyl chloride, two benzene residues are connected together by three carbon atoms. The free acid, which crystallizes in needles, M. Pt. 109°, is split up into CO_2 and the di-ketone **Dibenzoyl-methane**, $(C_6H_5CO)_2{=}CH_2$, when boiled with water. In the latter, a solid substance which boils without decomposition, the hydrogen of the methylene group is replaceable by metals (through the influence of the two carbonyls), so that the compound dissolves in alkalies and is again thrown down by acids. By the further action of benzoyl chloride upon its sodium compound, we obtain **Tribenzoyl-methane**, $(C_6H_5.CO)_3CH$.

Vulpic acid, $C_{19}H_{14}O_5$, a lichen acid, is related to the above compounds.

Tetraphenyl-ethane, $(C_6H_5)_2{=}CH—CH{=}(C_6H_5)_2$ (large prisms), and **Tetraphenyl-ethylene**, $(C_6H_5)_2{=}C{=}C{=}(C_6H_5)_2$ (fine needles), are also related to dibenzyl; both of these go into benzophenone upon oxidation.

COMPOUNDS WITH CONDENSED BENZENE NUCLEI.

That portion of coal tar which boils at a high temperature contains a number of higher hydrocarbons, among which may be especially mentioned naphthalene, $C_{10}H_8$, anthracene,

$C_{14}H_{10}$, and its isomeride phenanthrene, $C_{14}H_{10}$. The first-named is found in the fraction between 180–200°, and the two latter in that between 340–360°.

These compounds are of more complex composition than benzene, the molecule of naphthalene differing from that of the latter by C_4H_2, and those of anthracene and phenanthrene from that of naphthalene by the same increment. They show however the most complete analogy to benzene as regards behaviour, so that almost exactly the same varieties of compounds may be derived from them as from benzene itself.

As a matter of fact they are undoubtedly benzene derivatives, anthracene yielding benzoic acid upon oxidation, naphthalene phthalic acid, and phenanthrene diphenic acid. From their modes of formation and behaviour it follows that in the building up of their molecules the benzene residues combine together in such a manner that 2 or (2 × 2) contiguous carbon atoms are common to both. For further details see pp. 500 and 509.

XXXI. NAPHTHALENE GROUP.

Naphthalene.

Naphthalene, $C_{10}H_8$, was discovered by *Garden* in 1820. It is contained in coal tar and crystallizes out from the fraction which distils over between 180–200°.

Formation. 1. By exposing a large number of carbon compounds to a red heat; thus, together with benzene, styrene, etc., by passing the vapours of methane, ethylene, acetylene, alcohol, acetic acid, etc. through red-hot tubes.

2. By leading the vapour of phenyl-butylene dibromide, $C_6H_5—CH_2—CH_2—CHBr—CH_2Br$, over quick-lime raised to a low red heat (*Aronheim*):

$$C_{10}H_{12}Br_2 = C_{10}H_8 + 2HBr + H_2.$$

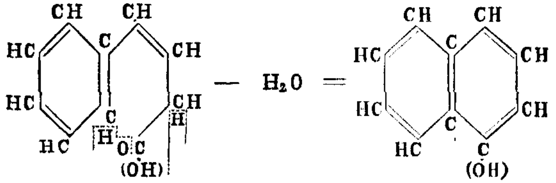
3. By the action of *o*-xylylene bromide (p. 366) upon the sodium compound of the symmetrical ethane-tetracarboxylic ether (p. 268), there results "Hydronaphthalene-tetracarboxylic ether," thus:

$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix} + \begin{matrix}Na—C(CO_2R)_2\\Na—\dot{C}(CO_2R)_2\end{matrix} = C_6H_4{<}\begin{matrix}CH_2—C(CO_2R)_2\\CH_2—\dot{C}(CO_2R)_2\end{matrix} + 2NaBr;$$

and from this latter, by the separation of the carboxyl groups and the excess of hydrogen, naphthalene (*Baeyer* and *Perkin*, B. **17**, 448).

4. α-Naphthol, $C_{10}H_7.OH$, is produced by the separation of water from phenyl-isocrotonic acid (*Fittig* and *Erdmann*, B. 16, 43), and yields naphthalene when heated with zinc dust. For further details, see below.

Constitution. That naphthalene contains a benzene nucleus, in which two hydrogen atoms occupying the ortho-position are replaced by the group $(C_4H_4)''$, follows not only from its oxidizability to phthalic acid, but also (*e.g.*) from its formation from *o*-xylylene bromide. And that the four carbon atoms of this group are linked to one another without branching is shown by the formation of α-napthol (as given above), from which it follows at the same time that the end C–atom of the side chain takes hold of the benzene nucleus already present, with the production of a new six-cornered ring:

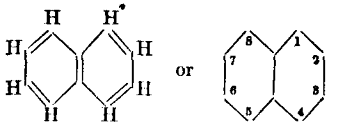


Phenyl-isocrotonic acid. α-Naphthol.

That there are actually two so-called "condensed" benzene nuclei present in the naphthalene molecule is a necessary consequence of the fact that phthalic acid or its derivatives ensue on the breaking up of the compound, not only from one but from both of the six-cornered rings.

For instance, α-nitro-naphthalene (p. 503) allows itself to be oxidized to nitro-phthalic acid, $C_6H_3(NO_2)(CO_2H)_2$; consequently the benzene ring to which the nitro-group is linked remains intact. But, on reducing the nitro-naphthalene to amido-naphthalene and oxidizing the latter, no amido-phthalic acid nor any oxidation product of it is obtained, but phthalic acid itself, a proof that this time the benzene nucleus which binds the amido-group has been destroyed, and that the other has remained intact (*Graebe*, 1880; for an analogous proof by him, see A. **149**, 20).

Naphthalene therefore receives the constitutional formula (*Erlenmeyer*, 1866):



This union of two benzene nuclei is accompanied by a modification of their properties, so that naphthalene and its derivatives differ characteristically from benzene in many respects. Such differences show themselves, for instance, between the naphthylamines and aniline, the naphthols and phenol; and also especially in the greater readiness with which the naphthalene derivatives are hydrogenized, the latter taking up as many as four atoms of hydrogen easily.

After such addition the hydrogenized nucleus is found to have entirely lost the characteristics of the benzene nucleus, and to have become very similar in properties to a radicle of the fatty series, whereas the (other) non-hydrogenized nucleus assumes the character of a benzene nucleus in its entirety (*Bamberger*). See the tetrahydro-naphthols, p. 505.

Properties. Naphthalene crystallizes in glancing plates which are insoluble in water, sparingly soluble in cold alcohol and ligroin, but readily soluble in hot alcohol and ether; M. Pt. 80°, B. Pt. 218°. It has a characteristic tarry smell, and is distinguished by the ease with which it sublimes and volatilizes with steam.

It yields a molecular compound, crystallizing in yellow needles, with picric acid, and takes up hydrogen far more readily than benzene does to form **Naphthalene dihydride**, $C_{10}H_8.H_2$, and **-tetrahydride**, $C_{10}H_8.H_4$, both of these being liquids of pungent odour which regenerate naphthalene again when heated. By the powerful action of hydriodic acid and phosphorus, the second benzene nucleus can also be made to take up hydrogen, so that a **hexahydride**, $C_{10}H_8.H_6$, and finally a **dekahydride**, $C_{10}H_8.H_{10}$, result. It likewise yields addition-products with chlorine more readily than benzene does, *e.g.* **Naphthalene dichloride**, $C_{10}H_8.Cl_2$, and **-tetrachloride**, $C_{10}H_8.Cl_4$ (M. Pt. 182°); the latter is oxidized to phthalic acid more easily than naphthalene itself, hence that acid is prepared from it on the large scale.

Naphthalene is principally used for the preparation of phthalic acid (for eosin, etc.), and of naphthylamines and naphthols (for azo-dyes); also for the carburation of illuminating gas. It is a powerful antiseptic, and is employed therapeutically.

Derivatives of Naphthalene.

The substitution products etc. of naphthalene may be mono- or di-derivatives, etc.

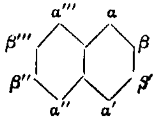
The mono-derivatives invariably exist in two isomeric forms, the α- and β-compounds, thus:

$C_{10}H_7Cl$ $\left.\begin{matrix}\alpha\text{-}\\ \beta\text{-}\end{matrix}\right\}$ Chloro-naphthalene. $C_{10}H_7NH_2$ $\left.\begin{matrix}\alpha\text{-}\\ \beta\text{-}\end{matrix}\right\}$ Naphthylamine.

$C_{10}H_7OH$ $\left.\begin{matrix}\alpha\text{-}\\ \beta\text{-}\end{matrix}\right\}$ Naphthol. $C_{10}H_7CH_3$ $\left.\begin{matrix}\alpha\text{-}\\ \beta\text{-}\end{matrix}\right\}$ Methyl-naphthalene.

As in the case of the benzene compounds, the existence of two series of mono-derivatives here has not only been established empirically, but it has also been proved (in a manner similar to that given on p. 340 *et seq.*) that in the naphthalene molecule two sets of hydrogen atoms (viz. α, α′, α″, α‴ and β, β′, β″, β‴) have an equal value as regards one another (but the atoms of the one set differ from those of the other), so that the α- and the β-positions occur severally four times, *i.e.* twice in each benzene nucleus (*Atterberg*).

The above constitutional formula for naphthalene satisfies these conditions admirably, since, according to it, the positions 1, 4, 5 and 8 are severally equal and also the positions 2, 3, 6 and 7, but not the positions 1 and 2. The conception that in the α-compounds the position 1, 4, 5 or 8 is occupied:



is due to *Liebermann* (A. **183**, 225), *Reverdin* and *Nolting* (B. **13**, 36), and *Fittig* and *Erdmann* (cf. the formation of α-naphthol given above).

With regard to the di-derivatives of naphthalene, a considerable number of isomerides of a good many are known; according to the naphthalene formula, ten are theoretically possible in each case when the two substituents are the same, and fourteen when they are different.

The position 1:8 (*i.e.* α:α‴) is termed the "*peri-*" position; it resembles the ortho- position to some extent.

Bromo-naphthalenes.

α-Bromo-naphthalene, which can be prepared directly, goes partially into the β-compound when heated with chloride of aluminium. Its bromine atom is somewhat more easily exchangeable than that of bromo-benzene.

Nitro-naphthalenes.

α-**Nitro-naphthalene**, $C_{10}H_7.NO_2$ (*Laurent*, 1835), results from the direct nitration of naphthalene. It forms yellow prisms, M. Pt. 61°, boils without decomposition, and goes into di-, tri- and tetra-nitro-naphthalenes upon further nitration. On reduction it is converted into α-naphthylamine.

The isomeric β-**Nitro-naphthalene** can be obtained indirectly by diazotizing β-naphthylamine, and acting on the product with sodium nitrite in presence of cuprous oxide (see p. 371); it crystallizes in bright yellow needles.

Naphthylamines; Naphthalene-sulphonic acids.

α-**Naphthylamine**, $C_{10}H_7.NH_2$ (*Zinin*), forms colourless needles or prisms readily soluble in alcohol; M. Pt. 50°, B. Pt. 300°. It can also be easily prepared by heating α-naphthol with the double compound of chloride of calcium and ammonia (while aniline can only be got from phenol in a similar manner with difficulty):

$$C_{10}H_7.OH + NH_3 = C_{10}H_7.NH_2 + H_2O.$$

It possesses a disagreeable fæcal-like odour, sublimes readily, and turns brown in the air. Certain oxidizing agents, such as ferric chloride, produce a blue precipitate with solutions of its salts, while others give rise to a red oxidation product; chromic anhydride oxidizes it to α-naphthoquinone. In other respects it is very like aniline. For the differences from aniline shown by it and by β-naphthylamine, cf. B. 23, 1124.

The isomeric β-**Naphthylamine**, $C_{10}H_7.NH_2$ (*Liebermann*, 1876), is most conveniently prepared by heating β-naphthol either in a stream of ammonia or with the double compound of zinc chloride and ammonia. It crystallizes in glancing mother-of-pearl plates, M. Pt. 112°, B. Pt. 294°, and has no odour. It is more stable than α-naphthylamine and is not coloured by oxidizing agents.

Both of these naphthylamines can be converted into tetrahydro-compounds by the action of sodium and alcohol (*i.e.* nascent hydrogen) upon

them. The resulting **Tetrahydro-α-naphthylamine** resembles its mother substance closely in most of its properties, *e.g.* it can be diazotized and has entirely assumed the character of aniline; the hydrogen atoms have entered the nucleus which does not contain the NH_2 group. It is termed *aromatic* or "*ar-*" tetrahydro-α-naphthylamine. **Tetrahydro-β-naphthylamine**, on the other hand, is not diazotized by nitrous acid but transformed into a very stable nitrite. Here it is the benzene nucleus containing the NH_2-group which has become hydrogenized; the compound has assumed the properties of an amine of the fatty series, and is termed *alicyclic* or "*ac-*" tetrahydro-β-naphthylamine. The α-compound is oxidizable to adipic acid (p. 247), and the β-compound to *o*-hydrocinnamo-carboxylic acid, $C_6H_4<^{CH_2-CH_2-CO_2H}_{CO_2H}$ (p. 467). Cf. *Bamberger* and others, B. **21**, 847, 1112, 1892; **22**, 625, 767; **23**, 876, 1124.

An **ac-Tetrahydro-α-** and an **ar-Tetrahydro-β-naphthylamine** have also been prepared.

From both naphthylamines there are derived, as in the benzene series, **Methyl-** and **Dimethyl-naphthylamines, Phenyl-α-** and **-β-naphthylamines** (which are of technical importance), **Nitro-naphthylamines**, Diamido-naphthalenes or **Naphthylene-diamines**, $C_{10}H_6(NH_2)_2$, **Diazo-compounds** (which are in every respect analogous to the diazo-compounds of benzene, especially in their capability of yielding azo-dyes), **Diazo-amido-compounds**, etc.

The **Diazo-amido-naphthalene**, $C_{10}H_7-N=N-NH-C_{10}H_7$, which results from the action of N_2O_3 upon α-naphthylamine, readily undergoes a molecular transformation (like the corresponding benzene compound) into **Amido-azo-naphthalene**, $C_{10}H_7-N=N-C_{10}H_6.NH_2$. This latter compound crystallizes in brownish-red needles with a green metallic glance, and can be diazotized, its diazo-compound yielding α-**Azo-naphthalene**, $C_{10}H_7-N=N-C_{10}H_7$ (red to steel-blue glancing prisms), when boiled with alcohol. This last can either not be prepared at all or only with great difficulty by the methods which hold good for azo-benzene.

Naphthalene-disulphonic acids, $C_{10}H_6(SO_3H)_2$.* Two isomeric β-β-acids (2:6 and 2:7) result upon treating naphthalene with concentrated sulphuric acid at 160°–200°, while an α-α-acid (1:5) is obtained with chloro-sulphonic acid, SO_3HCl, in the cold, and the α-β-acid (1:6) from the β-mono-sulphonic acid in a similar manner.

Naphthylamine-mono-sulphonic acids, $C_{10}H_6(NH_2)(SO_3H)$. Eleven isomers of these are known (7 α- and 4 β-). **Naphthionic acid** ($NH_2:SO_3H$ = 1:4) results upon sulphurating α-naphthylamine; it is employed in the preparation of azo-dyes, as are also several of its isomers and various **Naphthylamine-disulphonic acids.** These last are partly obtained directly from α- or β-naphthylamine, and partly by nitrating and amidating the naphthalene-sulphonic acids.

* For Naphthalene-mono-sulphuric acids, see *Appendix*, p. 567.

Naphthols.

α- and **β-Naphthols**, $C_{10}H_7.OH$, which are present in coal tar, can be easily prepared, not only from the naphthalene-sulphonic acids as above, but also by diazotizing the naphthyl-amines. They crystallize in glancing plates of a phenolic odour, and are readily soluble in alcohol and ether but only sparingly in hot water. α-Naphthol (*Griess*, 1866) has the M. Pt. 95° and B. Pt. 282°, while β-naphthol (*Schäffer*, 1869) has the M. Pt. 122° and B. Pt. 288°; both of them are readily volatile. They possess a phenolic character but nevertheless resemble the alcohols of the benzene series more than the phenols, their hydroxyl groups being far more capable of reaction than those of the latter, *e.g.* being readily exchange-able for NH_2 (see above). β-Naphthol is an antiseptic.

ar-Tetrahydro-α-naphthol, $C_{10}H_7.H_4.(OH)$, results upon hydrogenizing α-naphthol; it has the character of a pure phenol, and not that of α-naph-thol. **Ar-** and **ac- tetrahydro-β-naphthols** are obtained together in an analogous manner from β-naphthol, the *ar*-compound corresponding to phenol and the *ac*-compound to the fatty alcohols in behaviour.

Ferric chloride oxidizes α-naphthol and β-naphthol, with production of violet and greenish colourations respectively, to **Di-naphthols**, $C_{20}H_{12}(OH)_2$, which correspond to the di-phenols (p. 476), and are derivatives of di-naphthyls (p. 507). The cautious oxidation of α-naphthol yields *o*-**Cinnamo-carboxylic acid**, $C_6H_4(CO_2H)—CH=CH—CO_2H$ (p. 467), and that of β-naphthol, *o*-carboxyl-phenyl-glyoxylic acid, $C_6H_4(CO_2H)—CO—CO_2H$.

Both of the naphthols yield **Ethyl ethers**, $C_{10}H_7.O.C_2H_5$, **Acetyl-naphthols**, $C_{10}H_7.O(C_2H_3O)$, etc.

Betol, *naphtho-salol*, $C_{10}H_7.O.CO—C_6H_4(OH)$, the salicylic ester of β-naphthol, is a colourless crystalline powder, M. Pt. 95°, and is used thera-peutically like salol. From the naphthols, as from the phenols, there are derived **Nitro-**, **Dinitro-**, **Trinitro-**, and **Amido-compounds**, etc. The calcium salt of **Dinitro-α-naphthol**, $C_{10}H_5(NO_2)_2.OH$, is known as *Martius*' yellow or naphthalene yellow, and its sulphonic acid, **Naphthol yellow S** or *fast yellow*, is also a valuable yellow dye.

Amido-naphthols, $C_{10}H_6(NH_2)(OH)$, result from the nitro-naphthols upon reduction; like the amido-phenols they are readily oxidized in the air (NH_2 : OH in the α-compound = 1 : 4, in the β-compound = 1 : 2.)

A number of **Naphthol-mono-, -di-,** etc. **sulphonic acids** are known, which are of great technical value; among these may be mentioned **1 : 4-Naphthol-sulphonic acid** (*Nevile* and *Winther*),

from naphthionic acid, the 2:8-acid (*Rumpf*), the β-Naphtho-disulphonic acids R (2 : 3 : 6) or "R-salt," and G (2 : 6 : 8) or "G-salt," the three last-named from β-naphthol, etc.

The sodium salt of an **Amido-β-naphthol-sulphonic acid** is used as a photographic developer under the name of *Eikonogen*.

A series of very important azo-dyes (see also under Benzidine) are produced by the action of diazo-compounds, and of diazo-naphthalene-sulphonic acids upon the naphthylamines and naphthols, and especially upon the sulphonic acids of these, *e.g.*:—

Benzene-azo-α-naphthylamine, $C_6H_5—N=N—C_{10}H_6.NH_2$;

Orange II., $C_6H_4(SO_3Na)—N=N—C_{10}H_6(OH)$ [β];

Ponceau 2 R, from diazotized xylidine and "R-salt" (see above);

Fast Red C ("*Echtroth*"), $C_{10}H_6(SO_3Na)—N=N—C_{10}H_5(OH)(SO_3Na)$, from naphthionic acid and α-naphthol-monosulphonic acid 1:4;

Biebrich Scarlet, $C_6H_4(SO_3Na)—N=N—C_6H_4—N=N—C_{10}H_6(OH)$, from amido-azo-benzene-sulphonic acid and β-naphthol;

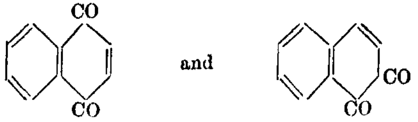
Brilliant Black, $C_{10}H_5(SO_3Na)_2—N=N—C_{10}H_6—N=N—C_{10}H_4(OH)(SO_3Na)_2$; from naphthylamine-disulphonic acid, α-naphthylamine and "R-salt."

Dioxy-naphthalenes; Naphthoquinones.

Various **Dioxy-naphthalenes,** $C_{10}H_6(OH)_2$, are known. Two of them, the hydro-naphthoquinones (α-, = 1:4 and β-, = 1:2) are oxidizable by chromic acid to compounds of a quinonic nature (p. 427), the naphthoquinones, just as hydroquinone itself is.

α-Naphthoquinone, $C_{10}H_6O_2$, also results from the oxidation of naphthalene, α-naphthylamine, α-amido-naphthol, etc. by chromic acid. It crystallizes in yellow rhombic tablets, M. Pt. 125°, and is the complete analogue of ordinary quinone, having a similar odour and being volatile with steam.

β-Naphthoquinone, which crystallizes in yellow-red plates and blackens when heated to 115°–120°, has no odour and is not volatile, being thus more like phenanthrene-quinone. These two compounds receive the formulæ:



α- β-Naphthoquinone

(see *Schultz*, "Theerfarben," 2d edition, p. 722), since they react with hydroxylamine to form oximes, the so-called **Iso-nitroso-naphthols,** compounds which are also obtained by the action of nitrogen trioxide upon the naphthols themselves.

α-Naphthoquinone is converted by chloride of lime into iso-naphthazarine, and β-naphthoquinone into a lactonic acid containing all the ten carbon atoms (a hexa-ring being broken in this case), from which iso-quinoline is obtainable (see this). Cf. B. 25, 888, 1138, 1168, and 1493.

γ- or **Peri-naphthoquinone.** Cf. B. 23, Ref. 635.

Oxy-naphthoquinones, $C_{10}H_5O_2(OH)$, are likewise known. The ordinary oxy-naphthoquinone is a hydroxyl derivative of α-naphthoquinone

(O:O:OH = 1:4:2); **Juglone** (yellow needles) is an isomeric oxy-naphthoquinone (O:O:OH = 1:4:5) which occurs in nut-shells and has also been prepared artificially (B. **20**, 934).

Dioxy-naphthoquinones, $C_{10}H_4O_2(OH)_2$:—(*a*) The **Naphthazarine** or "alizarin black" of commerce, a valuable dye which is prepared by acting upon α-dinitro-naphthalene with zinc and sulphuric acid, comports itself like the alizarin dyes; it is the "alizarin" of the naphthalene series; (*b*) **Iso-naphthazarine** (see p. 506).

Homologues of Naphthalene and Hydrocarbons related to it; Carboxylic Acids.

α- and **β-Methyl-naphthalenes**, $C_{10}H_7.CH_3$, and also the **Dimethyl-naphthalenes**, $C_{10}H_6(CH_3)_2$, are present in coal tar. They may be prepared synthetically by methods analogous to those applicable to the homologues of benzene.

The **Naphthoic acids**, $C_{10}H_7.(CO_2H)$, can be obtained by saponifying the cyano-naphthalenes and also by the other synthetical methods given on p. 441 *et seq.*; *they crystallize in fine needles sparingly soluble in hot* water, and break up into naphthalene and CO_2 when distilled with lime. From them there are derived the **Oxy-naphthoic acids**, $C_{10}H_6(OH)(CO_2H)$, which are related to salicylic acid or its isomers. Among the **Naphthalene-dicarboxylic acids**, $C_{10}H_6(CO_2H)_2$, which are known may be mentioned **Naphthalic acid** (1:8), which at a somewhat high temperature yields an anhydride similar to phthalic anhydride.

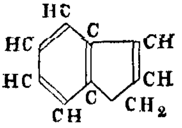
Phenyl-naphthalene, $C_{10}H_7(C_6H_5)$, has also been prepared; it is a compound built up of a naphthalene and of a benzene nucleus, and is therefore analogous to diphenyl, $C_6H_5—C_6H_5$. The same applies to:

Di-naphthyl, $C_{10}H_7—C_{10}H_7$, which yields derivatives (*e.g.* the di-naphthols, see p. 505) analogous to those of diphenyl. The three modifications which are theoretically possible, the α-α-, β-β-, and α-β-compounds, are known.

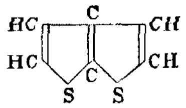
Another derivative of naphthalene is **Acenaphthene**, $C_{12}H_{10} = C_{10}H_6\langle{}^{CH_2}_{CH_2}$ (1:8), which is found in coal tar. It crystallizes in colourless prisms, M. Pt. 95°, B. Pt. 277°, and yields naphthalic acid on oxidation.

Appendix. Indene; Thiophtene.

The two following compounds possess a constitution similar to naphthalene:—



Indene, $=C_9H_8$.



Thiophtene, $=C_6H_4S_2$.

The first of these appears as resulting from the fusion of a benzene- with a penta-methylene ring, and the second in an analogous manner from two thiophene rings. **Indene** or *indo-naphtene* is present in coal tar (*Krämer*

and *Spilker*, B. **23**, 3276). It forms a clear colourless oil, B. Pt. 180°, which is resinified by concentrated sulphuric acid. Reduction by sodium and alcohol converts it into **Hydrindene**, C_9H_{10} (B. Pt. 176°), while nitric acid oxidizes it to phthalic acid. Many derivatives of it are known and have been prepared synthetically (cf. *e.g.* A. **247**, 129; B. **22**, 1830; **23**, 1881, 1887, Ref. 502).

Thiophtene is obtained by heating citric acid with phosphorus trisulphide; it is an oily liquid, B. Pt. 225° (B. **19**, 2444).

XXXII. THE ANTHRACENE AND PHENANTHRENE GROUPS.

A. Anthracene.

Anthracene, $C_{14}H_{10}$ (*Dumas* and *Laurent*, 1832; *Fritzsche*, 1857). *Formation.* 1. Together with benzene and naphthalene by the destructive distillation of coal and, generally, by the pyrogenous reactions which give rise to these products, *e.g.* by passing CH_4, C_2H_6, C_2H_2, the vapour of alcohol, etc. through red-hot tubes (cf. p. 499).

2. By heating *o*-tolyl-phenyl ketone with zinc dust (B. **7**, 17):

$$C_6H_4\left\langle\begin{matrix}CO\\CH_3\end{matrix}\right. \searrow C_6H_5 = C_6H_4\left\langle\begin{matrix}CH\\ \dot{C}H\end{matrix}\right\rangle C_6H_4 + H_2O.$$

3. Together with dibenzyl, by heating benzyl chloride with water to 200° (B. **7**, 276):

$$4C_6H_5{-}CH_2Cl = C_{14}H_{10} + C_{14}H_{14} + 4HCl.$$

4. From *o*-bromo-benzyl bromide and sodium in ethereal solution; here hydro-anthracene is at first formed, and this is converted by oxidation (which is partly spontaneous during the above reaction) into anthracene (B. **12**, 1965):

$$C_6H_4\left\langle\begin{matrix}Br\\CH_2Br\end{matrix}\right. + \begin{matrix}BrCH_2\\Br\end{matrix}\right\rangle C_6H_4 + 4Na = C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_4 + 4NaBr;$$

$$C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_4 - H_2 = C_6H_4\left\langle\begin{matrix}CH\\ \dot{C}H\end{matrix}\right\rangle C_6H_4.$$

5. By heating benzene with symmetrical tetrabromo-ethane and aluminic chloride (B. **16**, 623):

$$C_6H_6 + \begin{matrix}BrCHBr\\Br\dot{C}HBr\end{matrix} + C_6H_6 = C_6H_4\left\langle\begin{matrix}CH\\ \dot{C}H\end{matrix}\right\rangle C_6H_4 + 4HBr.$$

6. When phthalic anhydride is heated with benzene and

chloride of aluminium, *o*-benzoyl-benzoic acid results, and from this, on heating with phosphoric anhydride, anthraquinone (*Behr* and *v. Dorp*, B. 7, 578); the latter goes into anthracene upon reduction with zinc dust:

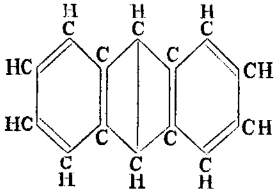
$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O + C_6H_6 = C_6H_4<\genfrac{}{}{0pt}{}{CO.C_6H_5}{CO.OH} = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4 + H_2O;$$

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4 + 3H_2 = C_6H_4<\genfrac{}{}{0pt}{}{CH}{CH}>C_6H_4 + 2H_2O.$$

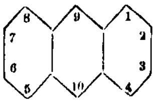
7. When a mixture of *m*-xylene and styrene is treated with concentrated sulphuric acid, there is formed *tolyl-phenyl-propane*, $CH_3-C_6H_4-CH_2-CH<\genfrac{}{}{0pt}{}{C_6H_5}{CH_3}$, which decomposes almost quantitatively into methane, hydrogen and methyl-anthracene on being strongly heated (B. 23, 3272).

8. From alizarin by means of zinc dust (see p. 513).

Constitution. From the above modes of formation and from its relation to anthraquinone, whose constitution follows *e.g.* from mode of formation 6, the anthracene molecule is seen to contain two benzene nuclei, C_6H_4, joined together by a middle group, C_2H_2. The carbon atoms of this middle group are likewise linked together, as is seen from mode of formation 5, and take up the *o*-position with regard to each other on one or other of the benzene nuclei (on one nucleus according to methods of formation 2 and 6, and on the other according to method 4; for further proofs of this, see *e.g. v. Pechmann*, B. 12, 2124). The constitution of anthracene is thus the following (*Graebe* and *Liebermann*, A. Suppl. 7, 313):



or



The two carbon atoms of the middle group thus form a new hexagon-ring with the carbon atoms of the benzene nuclei to which they are linked, so that anthracene may also be looked upon as being built up by the conjunction of three benzene nuclei. Besides the formula $C_6H_4<\genfrac{}{}{0pt}{}{CH}{CH}>C_6H_4$, the "quinoid" formula $C_6H_4\lessgtr\genfrac{}{}{0pt}{}{CH}{CH}>C_6H_4$ has also to be taken into consideration (*Armstrong*, Proc. Chem. Soc. for 1890, p. 101).

As regards combination with hydrogen, the same applies here as to naphthalene, two hydrogen atoms being readily added on at 9 and 10 (see

fig. above); the middle or "meso" ring thus shows a more or less aliphatic character, while both outer rings have entirely the character of benzene.

Properties and Behaviour. Anthraçene crystallizes in colourless plates which show a magnificent blue fluorescence. It is insoluble in water and only sparingly soluble in alcohol and ether, but readily so in hot benzene; M. Pt. 213°, B. Pt. above 351°. With picric acid it yields an addition-compound crystallizing in beautiful red needles.

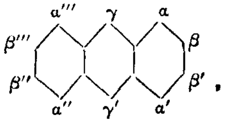
Anthracene is transformed by sunlight into (the polymeric) **Para-anthracene**, $(C_{14}H_{10})_2$. It takes up in the first instance two atoms of hydrogen when reduced (*e.g.* by hydriodic acid and phosphorus), with the formation of **Anthracene dihydride**, $C_{14}H_{10}.H_2$ (see above, mode of formation 4). This latter crystallizes in white plates, readily soluble in alcohol, M. Pt. 107°; it sublimes easily and distils without decomposition, but goes back into anthracene at a red heat or when warmed with concentrated sulphuric acid. It has the constitution:

$$C_6H_4{<}\substack{CH_2\\CH_2}{>}C_6H_4.$$

Further addition of hydrogen yields the hydrides $C_{14}H_{16}$ and, finally, $C_{14}H_{24}$.

Derivatives of Anthracene.

Theoretically three isomeric mono-derivatives are possible in each case, viz., the α-, β- and γ-compounds:



since, in the graphical formula given on the preceding page, $1 = 4 = 5 = 8 = \alpha$, $2 = 3 = 6 = 7 = \beta$, and $9 = 10 = \gamma$. The observed facts are in complete accordance with this.

The position of the substituting group can usually be determined either by the behaviour of the substance in question upon oxidation, *e.g.* if it be in the γ-position it will be eliminated with the formation of anthraquinone; or it is arrived at from the synthesis of the compound, *e.g.* in the case of alizarin, whose formation from pyrocatechin and phthalic acid shows that its two hydroxyls are contained in one and the same benzene nucleus.

Anthraquinone, $C_6H_4(CO)_2C_6H_4$, in which the hydrogen atoms 9 and 10 are replaced by two atoms of oxygen, only yields two isomeric mono-derivatives in each case. Isomeric di-derivatives may exist in very large number.

Summary of the most important derivatives of Anthracene.

$C_{14}H_9Cl$, $C_{14}H_8Cl_2$, $C_{14}H_8Br_2$ — Chloro-, Dichloro-, and *Dibromo-Anthracenes* (γ)	$C_{14}H_9.NH_2$, *Anthramine* (β).
$C_{14}H_9.NO_2$, $C_{14}H_8(NO_2)_2$ — Mono- and Dinitro-anthracenes (γ).	$C_{14}H_9.SO_3H$ — β-Anthracene-sulphonic acid.
	$C_{14}H_8(SO_3H)_2$ — α- and β-Anthracene-disulphonic acids.

$C_{14}H_9(OH)$, *Oxy-anthracenes :*

$C_6H_4<^{CH}_{CH}>C_6H_3.OH$ α, β Anthrol.	$C_6H_4<^{CH}_{C(OH)}>C_6H_4$, Anthranol (γ).
$C_6H_4<^{CH_2}_{CO}>C_6H_4$, Anthrone.	$C_6H_4<^{CH_2}_{CH(OH)}>C_6H_4$, Hydranthranol (γ).

$C_{14}H_8(OH)_2$, *Dioxy-anthracenes :*

$C_6H_4<^{C(OH)}_{C(OH)}>C_6H_4$, Anthra-hydroquinone (isomers : Rufol, Flavol, Chrysazol.)

$C_{14}H_8O_2$, *Anthraquinone :*

$C_{14}H_7O_2(SO_3H)$, $C_{14}H_6O_2(SO_3H)_2$ — Anthraquinone-mono- and disulphonic acids.	$C_6H_4<^{CH(OH)}_{CO}>C_6H_4$, Oxanthranol.

$C_{14}H_7O_2(OH)$, *Oxy-anthraquinones :*

$C_6H_4(CO)_2C_6H_3(OH)$: α = Erythro-oxy-, β = Oxy-anthraquinone.

$C_{14}H_6O_2(OH)_2$, *Dioxy-anthraquinones :*

$C_6H_4(CO)_2C_6H_2(OH)_2$: αβ = **Alizarin**, αα′ = Quinizarin, αβ′ = Purpuroxanthine, etc.

$C_6H_3(OH)(CO)_2C_6H_3(OH)$: Anthraflavic acid, Iso-anthraflavic acid, Anthrarufin, Chrysazin, etc.

$C_{14}H_5O_2(OH)_3$, *Trioxy-anthraquinones :*

$C_6H_4(CO)_2C_6H(OH)_3$: αβα′ = **Purpurin.**

Isomers : Flavo-purpurin, Anthra-purpurin, etc.

Tetroxy-anthraquinones: Anthrachrysone, Rufiopin, Quinalizarin.

Hexoxy-anthraquinones: Hexoxy-anthraquinone, Rufigallic acid.

$C_{14}H_9(CH_3)$, Methyl-anthracenes.	$C_{14}H_8(CH_3)_2$, Dimethyl-anthracenes.
$C_{14}H_9(C_6H_5)$, Phenyl-anthracene, etc.	$C_{14}H_9(CO_2H)$, Anthracene-carboxylic acids (α, β, γ).
$C_6H_4<^{CH_2}_{CHR}>C_6H_4$, Alkyl-hydro-anthracenes.	$C_6H_4<^{CH_2}_{CR(OH)}>C_6H_4$, Alkyl-hydranthranols.
$C_6H_4<^{C(OH)}_{[illegible]}>C_6H_4$, Phenyl-anthranol	$C_6H_4<^{CO}_{[illegible]}>C_6H_4$, Phenyl-oxanthranol.

Substitution products are obtained directly from these compounds; they yield anthraquinone upon oxidation, and therefore contain the halogen in the γ-position.

β-Anthramine, $C_{14}H_{11}N$, is obtained from β-anthrol, $C_{14}H_{10}O$, and ammonia, anthrol from anthracene-sulphonic acid and potash, and the last-named acid by the reduction of β-anthraquinone-mono-sulphonic acid. α- and β-Dioxy-anthracenes are prepared by fusing the sulphonic acids with potash, and the following substances, which stand midway between hydro-anthracene and anthraquinone, viz. hydranthranol, oxanthranol, anthranol and anthra-hydroquinone (*Liebermann*), by the more or less energetic reduction of anthraquinone. The oxy-anthracenes appear to be also present in coal tar. The phthalidines result from the action of concentrated sulphuric acid upon the *phthalines* (p. 494; cf. also B. **18**, 2150), thus:

$$C_6H_4{<}^{CH(C_6H_5)}_{CO.OH}{\searrow}C_6H_5 - H_2O = C_6H_4{<}^{C(C_6H_5)}_{C(OH)}{>}C_6H_4$$

Triphenyl-methane-carboxylic acid. Phenyl-anthranol;

they are oxidizable to the phthalideïns, *e.g.* Coeruleïn (p. 496). γ-Alkylated anthracenes are also produced by the elimination of the elements of water from the alkylated hydranthranols, which in their turn are obtained from hydranthranol by acting upon it with alkyl iodide and potash; while γ-phenyl-anthracene is got by heating phenyl-anthranol (a phthalidine) with zinc dust. For isomeric alkyl-anthracenes, see below. Anthraquinone and its oxy-compounds are of especial importance.

Anthraquinone, $C_{14}H_8O_2$ (*Laurent*, 1834). *Formation* as given above. It is easily obtained by oxidizing anthracene with chromic acid mixture (which is the method followed on the large scale), or with chromic anhydride and glacial acetic acid, and is also produced when calcium benzoate is distilled.

It crystallizes in yellow prisms or needles which are soluble in hot benzene, sublime with great readiness, and are exceedingly stable as regards oxidizing agents; M. Pt. 285°. Hydriodic acid at 150° reduces it either to anthracene or its di-hydride, while fusion with potash converts it into benzoic acid. It possesses more of a ketonic than of a quinonic character (*Zincke, Fittig*), not being reduced by sulphurous acid, and it gives an oxime with hydroxylamine.

It yields (mono- and di-) bromo-, nitro- and sulpho-compounds. **Anthraquinone-β-mono-sulphonic-acid** crystallizes in yellow tablets; of the **Di-sulpho-acids** we are acquainted with two which are formed directly from anthraquinone, and two which are produced by the oxidation of the anthracene-disulphonic acids.

Fusion of the sulphonic acids with potash does not generally yield the analogous oxy-compounds in theoretical quantity, oxygen being usually absorbed from the air at the same time; thus the mono-sulphonic acids yield mono- and dioxy-, and the di-sulphonic acids di- and trioxy-anthraquinones. In practical working the amount of chlorate of potash required is added to the "melt." Prolonged fusion with potash gives rise to decomposition into (oxy-) benzoic acids.

Various **Oxy-anthraquinones** can also be prepared by the synthetical mode of formation 6, p. 508, which applies in the case of anthraquinone, viz., from phthalic anhydride and the mono- or dioxy-benzenes (*Baeyer* and *Caro*, B. **7**, 792; **8**, 152), *e.g.*:

$$C_6H_4<{}^{CO}_{CO}>O + C_6H_4(OH)_2 = C_6H_4<{}^{CO}_{CO}>C_6H_2(OH)_2 + H_2O;$$

phenol yields by this method the two oxy-anthraquinones (yellow needles), pyro-catechin (1 : 2) yields alizarin, hydroquinone yields quinizarin, and so on. They are further produced by fusing chloro- and bromo-anthraquinones with potash, while *m*-oxy-benzoic acid can be converted directly by sulphuric acid into anthraflavic acid, water being separated (see Summary). Cf. A. **240**, 245.

Alizarin, $C_{14}H_8O_4$, is the most important constituent of the beautiful red dye of the madder root (Rubia tinctorum), which has been known for ages, being present in the latter as the readily decomposable glucoside, Ruberythric acid, $C_{26}H_{28}O_{14}$ (p. 560); in addition to alizarin, madder also contains purpurin. The preparation of alizarin from anthracene, with the intermediate formation of anthraquinone mono-sulphonic acid (mentioned above), which was first introduced in 1871 (*Graebe* and *Liebermann, Caro, Perkin*, B. **3**, 359; A. **160**, 130), depends upon an observation made by *Graebe* and *Liebermann* in 1868 (B. **1**, 49; A. Suppl. **7**, 297), that alizarin is reduced to anthracene when strongly heated with zinc dust.

It crystallizes in magnificent red prisms or needles of a glassy lustre, which melt at 289° and can be sublimed, dissolves readily in alcohol and ether, only sparingly in hot water, but, as a phenol, very easily in alkalies to a violet-red solution. It yields insoluble coloured compounds—the so-called "lakes"

—with metallic oxides, the alumina and tin lakes being of a magnificent red colour, iron lake violet-black, and lime lake blue. In the Turkey Red manufacture, for instance, the materials to be dyed are previously mordanted with acetate of alumina or with "ricinoleic-sulphuric acid" (see p. 233).

Anthrarobin, *dioxy-anthranol*, $C_6H_4<\begin{matrix}C(OH)\\CH\end{matrix}>C_6H_2(OH)_2$, is obtained by reducing alizarin with ammonia and zinc dust. It is a yellowish-white powder which is reconverted into alizarin on oxidation; on account of its reducing properties it is used in skin diseases.

Nitrogen tetroxide, N_2O_4, converts alizarin into **β-Nitro-alizarin** or Alizarin orange, $C_{14}H_7(NO_2)O_4$, a yellowish-red dye; and this latter, when treated with glycerine and sulphuric acid (the *Skraup* reaction, p. 531), yields **Alizarin blue**, $C_{17}H_9NO_4$ (see Quinoline), which is likewise a valuable blue dye, being used chiefly in the form of the $NaHSO_3$-compound.

Purpurin, Anthrapurpurin, and Flavopurpurin are also valuable dyes which are manufactured on a large scale; the same applies to the isomeric compound **Anthragallol** or "anthracene brown," $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)_3$, which is prepared by acting on a mixture of gallic and benzoic acids with concentrated sulphuric.

Alizarin-bordeaux, *quinalizarin* or *tetroxy-anthraquinone*, $C_{14}H_4O_2(OH)_4$ (cf. B. **23**, 3739), results from alizarin as an easily saponifiable sulphuric ester by the action of fuming sulphuric acid of high percentage. On oxidation it yields:

Penta- and Hexoxy-anthraquinones ("alizarin cyanines"), colours which dye a violet-blue with a chrome mordant (cf. J. pr. Ch. **43**, 237, 246). Related to these are the:

Anthracene Blue dyes, which are produced from α-α''-dinitro-anthraquinone by treating it successively with fuming and then with ordinary sulphuric acid; they yield blue tints with chrome mordants. A hexoxy-anthraquinone can also be prepared directly from anthraquinone by oxidation with sulphuric anhydride.

According to *v. Kostanecki* the colouring power of these compounds is connected with the presence of two hydroxyls in the ortho-position to one another.

Closely related to the anthracene dyes in properties is the yellow dye **Galloflavin**, $C_{13}H_6O_9$, which is obtained by exposing an alkaline solution of gallic acid to the action of the air (*Bohn* and *Graebe*, B. **20**, 2327).

Homologues of Anthracene.

(See *e.g.* mode of formation 7.)

There are also present in coal tar:

1. **Methyl-anthracene** (either α- or β-), $C_{14}H_9.CH_3$, which resembles anthracene and is oxidizable to methyl-anthraquinone; M. Pt. 199°.

2. **Dimethyl-anthracene**, $C_{14}H_8(CH_3)_2$, M. Pt. 224°–225°; isomers of this compound have been prepared synthetically.

The three **Anthracene-monocarboxylic acids** which are theoretically possible and also some **Anthracene-dicarboxylic acids** are likewise known.

B. Phenanthrene.

Phenanthrene, $C_{14}H_{10}$ [*Fittig* and *Ostermeyer* (1872), A. **166**, 361]. This hydrocarbon is found accompanying anthracene in coal tar. It crystallizes in colourless glancing plates, and dissolves in alcohol more readily than anthracene (with a blue fluorescence); M. Pt. 103°, B. Pt. 340°. It may be separated from anthracene by partial oxidation, the latter being the first to be attacked, and subsequent distillation. Oxidizing agents convert it into diphenic acid (p. 479). It is employed in the manufacture of printer's black.

Formation. 1. By leading the vapour of toluene, stilbene, dibenzyl or *o*-ditolyl through a red-hot tube, thus:

$$\begin{array}{l} C_6H_4-CH_3 \\ | \\ C_6H_4-CH_3 \end{array} = \begin{array}{l} C_6H_4-CH \\ | \qquad\ \ \| \\ C_6H_4-CH \end{array} + 2H_2.$$

o-Ditolyl. Phenanthrene.

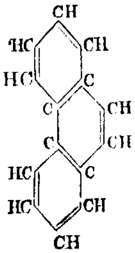
2. Together with anthracene from *o*-bromo-benzyl bromide and sodium.

3. By distilling morphine with zinc dust.

Constitution. The formation of phenanthrene from *o*-ditolyl, and its oxidation to diphenic acid, $\begin{array}{l} C_6H_4-CO_2H \\ C_6H_4-CO_2H \end{array}$, show that it is a diphenyl derivative and *that it contains one C-atom linked to each benzene nucleus*; this carbon atom is joined to the corresponding one by a double bond, as is shown *e.g.* by its formation from stilbene, $\begin{array}{l} C_6H_5-CH \\ C_6H_5-CH \end{array}$, a reaction completely analogous to the preparation of diphenyl from benzene. Since diphenic acid is a di-ortho-diphenyl-dicarboxylic acid (*Schultz*, A. **196**, 1; **203**, 95), phenanthrene is also a di-ortho-derivative and possesses the following constitution:

$$\begin{array}{l} C_6H_4-CH \\ | \qquad\ \ \| \\ C_6H_4-CH \end{array}$$

or



According to the above formula, the two CH-groups form a new hexagon ring with the two carbon atoms of both benzene nuclei of the

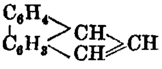
diphenyl to which they are linked, so that phenanthrene—like anthracene—may be looked upon as the product of the coalition of three benzene nuclei, or of one naphthalene and one benzene nucleus.

We are likewise acquainted with addition and substitution products of phenanthrene, *e.g.* a tetrahydride, nitro-, amido-, cyano- and oxy-compounds, and sulphonic and carboxylic acids. **Phenanthrol**, $C_{14}H_9(OH)$, is an oxy-phenanthrene, and **Phenanthrene-hydroquinone**, $C_{14}H_8(OH)_2$, a dioxy-compound which goes upon oxidation into:

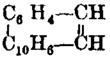
Phenanthrene-quinone, $\begin{array}{l} C_6H_4-CO \\ | \qquad\quad | \\ C_6H_4-CO \end{array}$, which latter may also be prepared directly from phenanthrene and chromic acid. It crystallizes in odourless orange needles which distil unchanged, but are not volatile with steam; M. Pt. 200°. Phenanthrene-quinone possesses the character of a di-ketone, reacting with hydroxylamine, sodium bisulphite, etc., but it can be reduced to the corresponding hydroquinone by sulphurous acid. It gives a bluish-green colouration with toluene containing thio-tolene, glacial acetic acid and sulphuric acid, which changes to violet after dilution and addition of ether, *i.e.* the ether becomes violet-coloured; this is the *Laubenheimer* reaction (see p. 327, also B. **17**, 1338).

C. Hydrocarbons of more complex nature.

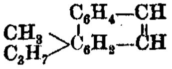
Fluoranthene, $C_{15}H_{10}$, **Pyrene**, $C_{16}H_{10}$, **Chrysene**, $C_{18}H_{12}$, and **Retene**, $C_{18}H_{18}$, are hydrocarbons which have been isolated from that portion of coal tar which boils at above 360°. Phenanthrene, pyrene and fluoranthene are also found in "Stupp" fat, *i.e.* the fat obtained as a bye-product from the working up of mercury ores in Idria. They all crystallize in white plates, sublime without decomposition, and are converted into the corresponding ketones upon oxidation. Their constitution is expressed by the following formulae (with regard to that of pyrene, see *Bamberger*, A. **240**, 147):



Fluoranthene.



Chrysene.



Retene.

Perhydro-retene, $C_{18}H_{32}$, is found native as *Fichtelite*, along with retene.

PYRIDINE DERIVATIVES, ALKALOIDS AND COMPOUNDS RELATED TO THEM.

The aromatic compounds which have been described up to now are derived from the mother hydrocarbons:

Benzene, C_6H_6, Naphthalene, $C_{10}H_8$, Anthracene, $C_{14}H_{10}$, etc.

But alongside of them we have to place several groups of very important nitrogenous compounds, which are derived from the mother substances:

Pyridine, C_5H_5N, Quinoline, C_9H_7N, Acridine, $C_{13}H_9N$, etc.

in precisely the same manner as the former are from benzene, etc., *i.e.* through the replacement of hydrogen by halogen, NO_2, NH_2, SO_3H, OH, CH_3, CO_2H, etc.

The difference in composition between these bases (among one another) is C_4H_2, this being the same as the difference between the mother hydrocarbons, from which they may be considered as being derived by the exchange of CH for N, thus:

$$C_6H_6 - CH + N = C_5H_5N.$$

Just as naphthalene and anthracene are benzene derivatives, so are quinoline and acridine derivatives of benzene on the one hand and of pyridine on the other; the latter is thus the mother base of all the classes of compounds which are now about to be described.

It may be compared with benzene in many points:

1. It is even more stable than benzene, and is further distinguished from the latter by a greater indifference towards the substituting reagents sulphuric and nitric acids and the halogens. The first of these sulphurates only at very high temperatures; nitro-pyridines are as yet unknown, as are also iodo-pyridines; while chloro- and bromo-pyridines have so far only been prepared in small number. Neither pyridine nor its carboxylic acids are affected by nitric acid, chromic acid, or permanganate of potash.

2. The behaviour of its derivatives is on the whole very like that of the derivatives of benzene. Thus its homologues (and also quinoline, etc.) are transformed into pyridine-carboxylic acids upon oxidation, and these acids yield pyridine when distilled with lime, just as benzoic acid yields benzene.

3. The isomeric relations are also precisely similar to those of the benzene derivatives. Thus the number of the isomeric mono-derivatives of pyridine is the same as that of the isomeric bi-derivatives of benzene, viz., three; and the number of the bi-derivatives of pyridine, with two atoms of one and the same substituent, the same as that of the benzene derivatives C_6H_3XXX', viz., six, and so on.

4. The products of reduction are likewise analogous. Just as hexahydro-benzene results from benzene, so do we obtain from pyridine (but more easily) hexahydro-pyridine or piperidine, $C_5H_{11}N$; further, just as naphthalene yields tetrahydro-naphthalene, so does quinoline (readily) tetrahydro-quinoline, $C_9H_{11}N$, and acridine (readily) (di-) hydro-acridine, $C_{13}H_{11}N$, which last is analogous to anthracene di-hydride. Here also, as in the case of the hydrides of the benzene series, further combination with hydrogen may take place, but there is likewise here a tendency to the reproduction of the original bases.

Consequently the *constitution* of these compounds is very similar to that of the benzene hydrocarbons. (For further details, see pp. 522 and 533.)

In contradistinction to the neutral benzene hydrocarbons, pyridine and its homologues, etc., are strong bases, most of them having a pungent odour; pyridine is readily soluble in water but quinoline only slightly so. They distil or sublime without decomposition, and form salts with hydrochloric and sulphuric acids which are for the most part readily soluble, while those with chromic acid, though often characteristic, are usually only sparingly soluble; also double salts with the chlorides of platinum, gold and mercury, most of which dissolve with difficulty, and so on.

Summary of several Pyridine and Quinoline Derivatives.

dine	C_5H_5N	*Quinoline*	C_9H_7N
ro-pyridine, etc.	C_5H_4NCl	Chloro-quinoline, etc.	C_9H_6NCl
		Amido-quinolines . .	$C_9H_6N(NH_2)$
dine-sulphonic id (β-)	$C_5H_4N(SO_3H)$	Quinoline-sulphonic acids	$C_9H_6N(SO_3H)$
pyridines (3) . .	$C_5H_4N(OH)$	*Oxy-quinolines* . . .	$C_9H_6N(OH)$
yl-pyridines . . (Picolines) (3)	$C_5H_4N(CH_3)$	*Methyl-quinolines* . . (Quinaldine, etc.)	$C_9H_6N(CH_3)$
ethyl-pyridines . (Lutidines)	$C_5H_3N(CH_3)_2$	Dimethyl-quinolines .	$C_9H_5N(CH_3)_2$
ethyl-pyridines .	$C_5H_2N(CH_3)_3$	Trimethyl-quinolines .	$C_9H_4N(CH_3)_3$
yl-pyridines . .	$C_5H_4N(C_3H_7)$	etc.	
dine-carboxylic ids (3)	$C_5H_4N(CO_2H)$	*Quinoline-carboxylic acids*	$C_9H_6N(CO_2H)$
dine-dicarboxylic ids (6)	$C_5H_3N(CO_2H)_2$	Quinoline-dicarboxylic acids	$C_9H_5N(CO_2H)_2$
line-carboxylic ids	$C_5H_3N(CH_3)(CO_2H)$	Quinaldine-carboxylic acids	$C_9H_5N(CH_3)(CO_2H$
yridine	$C_{10}H_{10}N_2$	Di-quinoline	$C_{18}H_{14}N_2$
yridyl	$C_5H_4N—C_5H_4N$	Di-quinolyline . . .	$C_9H_6N—C_9H_6N$
yl-pyridines . .	$C_5H_4N(C_6H_5)$	Phenyl-quinolines . .	$C_9H_6N(C_6H_5)$
ridine	$C_5H_{11}N$	*Tetrahydro-quinoline* .	$C_9H_{11}N$

As bases they are tertiary, and therefore cannot (*e.g.*) be acetylated; they combine with methyl iodide to quaternary compounds.

Pyridine, quinoline and many of their homologues (and also acridine) are found in coal tar and in bone oil (oleum Dippelii animale), from which they can be separated by the addition of acids; nevertheless they cannot, speaking generally, be obtained chemically pure even by repeated

fractionation. To prepare them pure, therefore, recourse must often be had to synthetical methods.

The quinoline and also the pyridine bases result from the distillation of most of the alkaloids which occur in nature, *e.g.* quinine, cinchonine and strychnine, with caustic potash, etc., and their carboxylic acids from the oxidation of these alkaloids. It follows from this that most of the latter are pyridine derivatives.

The **Alkaloids** are vegetable bases, most of which exert an intensely poisonous or curative action; they are therefore of great medicinal importance. They will be treated of shortly here, partly under the pyridine and quinoline derivatives, and partly (where their relation to these is as yet only slightly known) in an appendix. Certain alkaloids (*e.g.* caffeine, p. 306, and choline, p. 211) belong moreover to other classes of compounds.

The designation "alkaloids" is now becoming limited to the vegetable bases which are derived from pyridine.

XXXIII. THE PYRIDINE GROUP, $C_nH_{2n-5}N$.

Cf. *Buchka's* "Chemie des Pyridins" (Vieweg, Brunswick).

The pyridine group comprises pyridine itself, together with its homologues, carboxylic acids and more nearly allied derivatives.

The homologues of pyridine which are obtained from coal tar and bone oil are known as Picoline (C_6H_7N), Lutidine (C_7), Collidine (C_8), Parvoline (C_9), Corindine (C_{10}), etc.; the fractions, however, whose empirical analyses agree with these formulae, do not represent chemical individuals, but are mixtures of isomeric and also in part of homologous bases.

All the homologues of pyridine are distinguished from pyridine itself, as those of benzene are from the latter, by the readiness with which they are oxidized to pyridine-carboxylic acids:

$$C_5H_3N(CH_3)(C_2H_5) \text{ yields } C_5H_3N(CO_2H)_2.$$

Formation. 1. The pyridine bases result from the destructive distillation of many nitrogenous organic substances, hence their presence in coal tar.

2. Lutidine is obtained, together with other bases, on distilling cinchonine with potash.

3. Pyridine results from the oxidation of its homologues to carboxylic acids, and the subsequent separation of carbon dioxide from the latter.

3*a*. Pyridine is got by oxidizing quinoline to quinolinic acid, $C_5H_3N(CO_2H)_2$, and then breaking up the carboxylic groups.

4. β-Methyl-pyridine results on distilling acrolein-ammonia (p. 150), and collidine in an analogous manner from crotonic aldehyde-ammonia or aldehyde-ammonia (p. 148) (*Baeyer*, A. 155, 283, 297).

5. Aldehydine, $C_8H_{11}N$, is produced by heating ethylidene chloride or bromide with alcoholic ammonia, and β-methyl-pyridine by heating glycerine with acetamide and phosphoric anhydride.

6. When aceto-acetic ether is warmed with aldehyde-ammonia, the ether of "Dihydro-collidine-dicarboxylic acid," *i.e.* a dihydride of trimethyl-pyridine-dicarboxylic ethyl ether, is produced (*Hantzsch*):

$$2C_6H_{10}O_3 + CH_3.CHO + NH_3 = C_5N(H_2)(CH_3)_3(CO_2R)_2 + 3H_2O.$$

This loses its two 'hydro-' hydrogen atoms when acted on by nitrous acid, and goes into collidine-dicarboxylic ether, $C_5N(CH_3)_3(CO_2R)_2$, from which collidine results on saponification and elimination of CO_2.

If, instead of aldehyde-ammonia, the ammonia compounds of other aldehydes are used, one obtains analogous bases of the formula:

$$C_5H_2N(CH_3)_2(C_nH_{2n+1}).$$

In the above reaction also a molecule of aceto-acetic ether may be replaced by one of aldehyde, when the mono-carboxylic ethers of dimethyl- etc. pyridine are formed, thus:

$$C_6H_{10}O_3 + 2CH_3.CHO + NH_3 = C_5H_2NH_2(CH_3)_2.CO_2R + 3H_2O.$$

This is a very important synthetical method (*Hantzsch*, A. **215**, 1, etc.).

7. When potassium-pyrrol, C_4H_4NK, is heated with $CHCl_3$, chloro-pyridine, C_5H_4ClN, results; and when with CH_2Cl_2, pyridine.

8. When the hydrochloride of penta-methylene-diamine, $C_5H_{10}(NH_2)_2$, is heated rapidly, piperidine is produced (*Ladenburg*, B. 18, 2956, 3100):

$$C_5H_{10}(NH_2)_2, HCl = C_5H_{11}N + NH_4Cl.$$

Pyridine is then obtained by heating the piperidine with concentrated sulphuric acid to 300° (*Königs*), or by heating it in acetic acid solution with acetate of silver to 180°:

$$C_5H_{11}N - 3H_2 = C_5H_5N.$$

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$$C_5H_{11}N - 3H_2 = C_5H_5N.$$

9. Piperidine hydrochloride is further produced by warming an aqueous solution of ε-chloro-amylamine (p. 211) (*Gabriel*, B. **25**, 421).

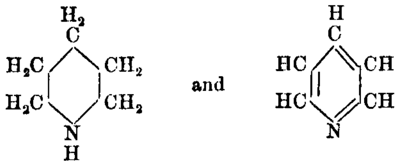
10. A *tetrahydro-picoline* is formed on treating δ-bromobutyl-methyl-ketone, $CH_2Br—(CH_2)_3—CO—CH_3$, with ammonia (*Lipp*, B. **25**, 2192).

11. The amides of citric acid, *e.g.* the monamide, $C_6H_7O_6(NH_2)$, yield citrazinic acid (dioxy-pyridine-γ-carboxylic acid) when warmed with H_2SO_4 (*Hofmann*); while acetone-dicarboxylic acid yields trioxy-pyridine (B. **19**, 2694).

12. Many compounds of the pyrone group (p. 529) are transformed into pyridine derivatives by the action of ammonia.

13. Conversely, homologues of pyridine are formed by heating the latter with alkyl iodide to 300° (*Ladenburg*), a reaction analogous to the production of toluidine from methyl-aniline.

Constitution. The constitution of piperidine and pyridine is expressed by the following formulæ (*Körner*, 1869):



(I.)

Piperidine. Pyridine.

That of piperidine follows from its formation from penta-methylene-diamine:

$$CH_2{<}{CH_2—CH_2—NH_2 \atop CH_2—CH_2—NH_2} = CH_2{<}{CH_2—CH_2 \atop CH_2—CH_2}{>}NH + NH_3.$$

Piperidine therefore contains a hexagon ring made up of one imido- and five methylene groups, and is a complete analogue of hexa-methylene; it may be designated penta-methylene-imine.

This constitution of piperidine receives further support from the products which are obtained from its decomposition, viz. (1) δ-amido-valeric acid on treating its benzoyl derivative with valeric acid (B. **24**, 3687), and (2) glutaric acid and ammonia by the action of hydrogen dioxide on piperidine itself (B. **25**, 2777).

The constitution of pyridine follows: 1. from its near relation to piperidine;

2. from the formation of pyridine-dicarboxylic acid by the oxidation of quinoline (see above):

$$C_9H_7N + O_9 = C_5H_3N(CO_2H)_2 + H_2O + 2CO_2,$$

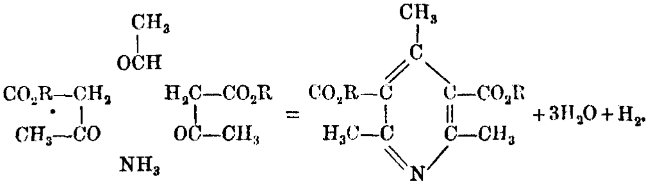
in conjunction with which are to be taken the proofs of the constitution of quinoline (p. 533);

3. from the perfect agreement with theory of the observed isomeric relations (see below);

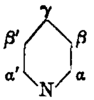
4. from the transformation of ethyl-pyridine into ethyl-benzene upon heating pyridine with ethyl iodide (A. **247**, 14).

The above constitutional formula of pyridine was first proposed by *Körner.*

The formation of collidine-dicarboxylic ether (p. 521) thus proceeds as follows (B. **18**, 1744):



Three isomeric mono-derivatives of pyridine are known in each case (p. 518). This agrees with the view that pyridine is a kind of mono-derivative of benzene in which, instead of H, a CH-group is replaced by N; the mono-derivatives of pyridine are thus comparable with the bi-derivatives of benzene, and are therefore three in number. They are designated as α-, β- and γ-derivatives of pyridine, as is shown in the following graphical formula:



(II.)

In order to determine the position of any given group, it is sought to exchange it for carboxyl; should picolinic acid result, it fills the α-position, and should nicotinic or iso-nicotinic, then it fills the β- or γ-position respectively, since in these acids the α-, β- and γ-positions of the carboxyl have been determined by special means. (See Monatsh. f. Chemie, **1**, 800; **4**, 436, 453, 595; B. **17**, 1518; **18**, 2967; **19**. 2432).

Di-derivatives of pyridine containing in the molecule two atoms of one and the same substituent can exist theoretically in six isomeric forms. As a matter of fact the six dicarboxylic acids, for example, are known (αα'-, αβ-, αγ-, αβ'-, βγ- and ββ'-; see (p. 527).

The above pyridine formula (II.) has the advantage over (I.) that it gives expression to the linking in ring form of the five carbon atoms and of the nitrogen, without rendering it necessary to take specially into

account the mode in which the fourth affinity of each carbon and the third affinity of the nitrogen are used (analogously to the hexagon formula of benzene, p. 344).

Besides *Körner's* formula another is frequently taken into consideration which, like *Dewar's* benzene formula (p. 348), shows a *para*-bond connecting the nitrogen atom with the γ-carbon atom, besides two double bonds between the carbon atoms $\alpha:\beta$ and $\alpha':\beta'$ (*Riedel, Bernthsen*). Of late, too, central linkings (three *para*-bonds) have been assumed in pyridine, this being in analogy with *Claus's* benzene formula (cf. p. 348; B. **24**, 3151).

The isomerism of picoline, C_6H_7N, with aniline, $C_6H_5.NH_2$, which repeats itself in their homologues, is also worthy of notice.

Pyridine.

Pyridine, C_5H_5N (*Anderson*, 1851), may be prepared from bone oil, and can be obtained chemically pure by heating its carboxylic acid with lime; the ferrocyanide is especially applicable for its purification, on account of its sparing solubility in cold water. It is also found in the ammonia of commerce. Pyridine is a liquid of very characteristic odour, miscible with water and boiling at 115°. When sodium is added to its hot alcoholic solution, hydrogen is taken up and piperidine, $C_5H_{11}N$, formed (*Ladenburg* and *Roth*, B. **17**, 513; see also p. 528). Pyridine is used as a remedy for asthma, and also in Germany for mixing with spirit of wine in order to render the latter duty-free.

When heated strongly with hydriodic acid, pyridine is converted into normal pentane.

The ammonium iodides, *e.g.* C_5H_5N, CH_3I, give a characteristic pungent odour when heated with potash, a fact which may be made use of as a test for pyridine bases; it depends upon the formation of alkylated dihydro-pyridines, *e.g.* **Dihydro-methyl-pyridine,** $C_5H_4.H_2.N(CH_3)$ (*Hofmann*, B. **14**, 1497).

Pyridine is polymerized by the action of metallic sodium to **Dipyridine,** $C_{10}H_{10}N_2$ (an oil, B. Pt. 286–290°), with the simultaneous production of *p*-**Dipyridyl,** $C_{10}H_8N_2$, $= C_5H_4N—C_5H_4N$ (long needles, M. Pt. 114°), a compound corresponding to diphenyl (p. 476); both of these yield iso-nicotinic acid upon oxidation. An isomeric *m*-**Dipyridyl** has also been prepared, which gives nicotinic acid when oxidized.

Pyridine can be brominated but not nitrated; it can also be sulphur-

ated, with the formation of β-pyridine-sulphonic acid, $C_5H_4N.(SO_3H)$, from which potassium cyanide produces **β-Cyano-pyridine**, $C_5H_4N.CN$, and fusion with potash β-oxy-pyridine.

The three **Oxy-pyridines**, $C_5H_4N(OH)$ (α-, β-, γ-), are best prepared by the separation of CO_2 from the respective oxy-pyridine-carboxylic acids. α-: M. Pt. 107°; β-: M. Pt. 124°; γ-: M. Pt. 148°. They possess the character *of phenols and are coloured red or yellow* by ferric chloride. As in the case of phloroglucin, so here also there is a tertiary as well as a secondary form to be taken into account, the former reminding one of the lactames and the latter of the lactimes; for instance, γ-oxy-pyridine may either have the "phenol" formula $C_2H_2<\genfrac{}{}{0pt}{}{C(OH)}{N}>C_2H_2$ or the "pyridone" formula $C_2H_2<\genfrac{}{}{0pt}{}{CO}{NH}>C_2H_2$, the latter of the two representing a keto-dihydro-pyridine. Both of the methyl derivatives, Methoxy-pyridine and Methyl-pyridone, which result from these two forms by the exchange of H (of the OH or NH respectively) for CH_3, are known (Monatsh. f. Chemie, **6**, 307, 320; B. **24**, 3144).

Trioxy-pyridine, $C_5H_5NO_3$. By the condensation of acetone-dicarboxylic ether with ammonia there is produced **Glutazine**, $C_5H_6N_2O_2$ (colourless plates soluble in alkali), which is converted by boiling hydrochloric acid into ammonia and trioxy-pyridine (yellowish microscopic prisms or needles). For its constitution see B. **19**, 2694; **20**, 2655.)

Homologues of Pyridine.

(Cf. *Ladenburg*, A. **247**, 1.)

Methyl-pyridines or Picolines, $C_5H_4N(CH_3)$. All the three picolines are contained in bone oil and probably also in coal tar. The β-compound results from acrolein-ammonia (p. 150) and also upon heating strychnine with lime. They are liquids of unpleasant piercing odour resembling that of pyridine, and they yield α-, β- or γ- pyridine-carboxylic acid when oxidized. α-: B. Pt. 129°; β-: B. Pt. 142°; γ-: B. Pt. 142°–144°.

Ethyl-pyridines, $C_5H_4N(C_2H_5)$, are also known, α-Ethyl-pyridine (B. Pt. 148°) being obtained by the breaking up of tropine.

Propyl- and Isopropyl Pyridines, $C_5H_4N(C_3H_7)$, have been carefully investigated on account of their near relation to conine. They are prepared as given at p. 522, 13. **Conyrine**, $C_8H_{11}N$ (liquid, B. Pt. 166°–168°), which results upon heating conine, $C_8H_{17}N$, with zinc dust, and which goes into conine again when treated with hydriodic acid, is α-normal propyl-pyridine.

α-Allyl-pyridine, $C_5H_4N(C_3H_5)$, is produced when α-picoline is heated with aldehyde:

$$C_5H_4N.CH_3 + OHC{-}CH_3 = C_5H_4N\,CH{=}CH{-}CH_3 + H_2O.$$

Reduction transforms it into inactive conine (B. Pt. 189 190°).

Dimethyl-pyridines or Lutidines, $C_5H_3N(CH_3)_2$. The presence of the three lutidines has been proved in bone oil and coal tar. For their synthetical formation see p. 521. α-γ-Lutidine boils at 157°, the α-α′-compound at 142°–143°, and the β-β′-compound at 169°–170°.

The **Collidines**, $C_8H_{11}N$, are isomeric with the propyl-pyridines.' Some of them are present in bone oil and can be prepared from cinchonine by distilling the latter with caustic potash (p. 521). The collidine (α-α′-γ) which is obtained from aceto-acetic ether and aldehyde-ammonia (p. 521), boils at 171°–172°. "Aldehydine" (from aldehyde, p. 521) is β′-ethyl-α-methyl-pyridine (B. **21**, 294).

α- and **β-Phenyl-pyridines**, $C_5H_4N(C_6H_5)$, are analogous to diphenyl. (See Monats. f. Chemie, IV., 456, 472.)

Pyridine-carboxylic acids.

(See Summary, also A. **241**, 1.)

The **Pyridine-mono-carboxylic acids**, $C_5H_4N(CO_2H)$, result from the oxidation of all the pyridine derivatives which contain only one (carbon-containing) side-chain, *i.e.* from methyl-, propyl-, phenyl-, etc. pyridines; also from the pyridine-dicarboxylic acids by the breaking up of one of the carboxyls, just as benzoic acid results from phthalic. It is the carboxyl which stands nearest to the nitrogen which is first eliminated here. Nicotinic acid is also produced by the oxidation of nicotine. They unite in themselves the characters of the basic pyridine and of an acid, and are therefore comparable with glycocoll. They yield salts with HCl, etc. and double salts with $HgCl_2$, $PtCl_4$, etc.; on the other hand they also form salts as acids, those with copper being frequently made use of for the separation of the acid.

For *Constitution* see *Skraup* and *Cobenzl*, Monats. f. Chemie, **4**, 436.

The α- acid is **Picolinic acid**; needles, M. Pt. 135°.
The β- „ **Nicotinic acid**; needles, M. Pt. 231°.
The γ- „ **Iso-nicotinic acid**; needles, M. Pt. (in sealed tube) 309°.

It is noteworthy that all three acids (and also *e.g.* the β-γ-dicarboxylic acid) readily yield up their nitrogen as ammonia when acted upon by sodium amalgam, being thereby transformed into unsaturated acids of the fatty series (*Weidel*, Monats. f. Chemie, 11, 501).

Pyridine-dicarboxylic acids, $C_5H_3N(CO_2H)_2$.

α-β- = **Quinolinic acid**, ...M. Pt. about 190°.
α-γ- = **Lutidinic acid**, ...M. Pt. 235°.
α-α'- = *Dipicolinic acid*,............M. Pt. 226°.
α-β'- = *Iso-cinchomeronic acid*, ...M. Pt. 236°.
β-β'- = *Dinicotinic acid*,............M. Pt. 323°.
β-γ- = *Cinchomeronic acid*, ...M. Pt. 249°.

Quinolinic acid (short glancing prisms), the analogue of phthalic acid, results from the oxidation of quinoline, just as phthalic acid does from naphthalene; cinchomeronic and iso-cinchomeronic acids from the oxidation of cinchonine and quinine. The constitution α-β- follows for quinolinic acid from its mode of formation.

The pyridine-mono- and di-carboxylic acids, which contain a carboxyl in the α-position, give a reddish-yellow colouration with ferrous sulphate.

Pyridine-tricarboxylic acids, $C_5H_2N(CO_2H)_3$, are obtained in a similar manner by the oxidation of quinine, cinchonine (**Carbo-cinchomeronic acid**), berberine (**Berberonic acid**), etc.

Pyridine-pentacarboxylic acid (from collidine-dicarboxylic acid) has no longer basic properties; it readily gives up CO_2.

Oxy-pyridine-carboxylic acids result from the action of ammonia upon many vegetable acids, especially upon carboxylic acids of pyrone derivatives (p. 529). Thus cumalic acid (from malic) is transformed by ammonia into:

α-**Oxy**-β-**nicotinic acid**, $C_5H_3N(OH)(CO_2H)$; colourless crystals, M. Pt. 303°.

γ-**Oxy-dipicolinic acid**, $C_5H_2N(OH)(CO_2H)_2$, is obtained from chelidonic acid (p. 529) in an analogous manner.

It is possible that similar reactions take place in the genesis of alkaloids from vegetable acids.

Citrazinic acid or α-α-*dioxy-isonicotinic acid* (see p. 522).

Hydro-derivatives of Pyridine.

According to theory, Hexa-, Tetra-, and Di-hydro-pyridines may exist. The first of these receive the generic name of "Piperidines," *e.g.* Pipecoline, $C_5H_{10}N(CH_3)$, Lupetidine, $C_5H_9N(CH_3)_2$, and Copellidine, $C_5H_8N(CH_3)_3$; while the tetra-hydro-compounds are termed "Piperideïns."

Dihydro-methyl-pyridine (see p. 524).

Dihydro-collidine-dicarboxylic acid (see p. 521).

Tetrahydro-pyridine or *piperideïn*. For synthesis, see B. 25, 2782.

α-**Pipecoleïn**, $C_6H_{11}N$, results from the action of bromine and soda solution upon piperidine; for a direct synthesis, see also p. 522.

α-Oxyethyl-n-methyl-tetrahydro-pyridine, $CH_3-NC_5H_7-CH_2-CH_2OH$ (obtained from α-pipecoleïn and formic aldehyde), is isomeric with tropine, although totally different from the latter.

Piperidine, $C_5H_{11}N$ (*Wertheim*, *Rochleder*, 1850), is a colourless liquid of peculiar odour slightly resembling that of pepper, and of strongly basic properties, readily soluble in water and alcohol; B. Pt. 106°. It forms crystalline salts.

It occurs in pepper in combination with piperic acid, $C_{12}H_{10}O_4$ (p. 463), in the form of the alkaloid **Piperine**, $C_{18}H_{18}NO_3$, $= C_5H_{10}N-C_{12}H_9O_3$, *i.e.* piperyl-piperidine, which crystallizes in prisms, M. Pt. 129°; from this latter it may be prepared by boiling with alkali.

For its formation from pyridine and from penta-methylene-diamine, see pp. 524 and 521.

Piperidine is a secondary amine; its imido-hydrogen is replaceable by alkyl and by acid radicles. When its vapour, mixed with that of alcohol, is led over zinc dust, homologous (ethylated) piperidines are formed.

As a secondary base piperidine yields, in the first instance, tertiary **n-methyl-piperidine**, $C_5H_{10}N(CH_3)$, on methylation, the latter then uniting further with methyl iodide to an ammonium iodide. The corresponding hydroxide does not decompose backwards upon distillation, but the ring is broken and a base of the fatty series results,—the so-called "dimethyl-piperidine," $C_7H_{15}N$. If this in its turn is treated with methyl iodide, an ammonium iodide is produced which, on distillation, gives off its nitrogen as tri-methylamine, and yields the hydrocarbon piperylene, C_5H_8 (p. 66). Cf. *Hofmann*, B. **14**, 660; *Ladenburg*, B. **16**, 2058; also A. **264**, 310.

Conine, dextro-rotatory *α-normal-propyl-piperidine*, $C_8H_{17}N$, $= C_5H_{10}N(C_3H_7)$, is the poisonous principle of hemlock (Conium maculatum). It is a colourless dextro-rotatory liquid of stupefying odour, slightly soluble in water; B. Pt. 167°. Hydriodic acid at a high temperature reduces it to normal octane, while nitric acid oxidizes it to butyric acid, and potassium permanganate to picolinic acid (hence the α-position).

Ladenburg has prepared it synthetically by reducing α-allyl-pyridine in alcoholic solution by means of sodium (B. **19**, 2578):

$$C_5H_4N(C_3H_5) + 4H_2 = C_5H_{10}N(C_3H_7).$$

In this reaction there is first formed the optically inactive α-normal-propyl-piperidine, which is broken up, by crystallization of the tartrate, into conine (dextro-conine) and a lævo-conine which resembles the other closely. The relations of these two bases to one another and to the inactive modification are the same as that of dextro- to lævo-tartaric acid and of

both of these to racemic acid (cf. B. **19**, 2574). Analogous relations hold good with regard to other α-alkyl-piperidines (A. **247**, 64, 80).

When treated thoroughly with methyl iodide, conine behaves similarly to piperidine (see above), the final product being conylene, C_8H_{14} (p. 66).

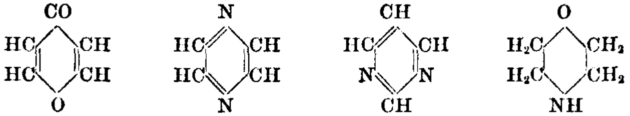
α-, β- and γ-**Coniceïns**, $C_8H_{15}N$, are peculiar bases which result from the (indirect) separation of hydrogen from conine. **Conydrine**, $C_{18}H_{17}NO$, an oxy-derivative, occurs along with conine in hemlock; it crystallizes in plates, M. Pt. 120°, B. Pt. 240°.

Nicotine, $C_{10}H_{14}N_2$, = $C_{10}H_8(H_6)N_2$, is the poisonous constituent of tobacco and the tobacco plant. It is a strong diatomic base, oily, readily soluble in water, alcohol and ether, and of a stupefying odour. It can be distilled unchanged in an atmosphere of hydrogen, but becomes rapidly brown in the air; B. Pt. about 250°.

Permanganate of potash oxidizes nicotine to nicotinic acid, whence it follows that the former is a β-pyridine derivative. It was formerly looked upon as hexahydro-dipyridyl, but according to *Pinner* (B. **26**, 292; cf., however, B. **26**, 628), it appears to be a pyridyl-n-methyl-pyrrolidine, $C_5H_4N.C_4H_7(NCH_3)$, in which the methyl-pyrrolidine is united to the β-carbon atom of the pyridine.

For *Tropine* and *Ecgonine*, two more complex pyridine derivatives, see p. 513.

Appendix: Pyrone; Pyrazine; Pyrimidine; Morpholine, etc.



Pyrone. Pyrazine. Pyrimidine. Morpholine.

1. **Pyrone**, *pyro-comane*, $C_5H_4O_2$ (a neutral compound, M. Pt. 32°, B. Pt. about 212°), and its position-isomer **Cumaline**, *α-pyrone*, $C_5H_4O_2$ (whose CO and O are next to one another in the ring, hence it is to be regarded as a δ-lactone), are the mother substances of the following compounds:

Comanic and **Cumalic acids**, $C_5H_3O_2(CO_2H)$, **Chelidonic acid**, $C_5H_2O_2(CO_2H)_2$, **Meconic acid**, $C_5HO_2(OH)(CO_2H)_2$, **Pyro-meconic acid**, $C_5H_3O_2(OH)$, etc. Chelidonic acid is found in celandine, and can be transformed into comanic acid and pyrone by the separation of carbon dioxide. Meconic acid occurs in opium and passes into pyro-meconic acid through loss of carbon dioxide. Cumalic acid results from malic acid, as given at p. 258.

When they are treated with ammonia these compounds exchange an oxygen atom for nitrogen, with the formation of pyridine derivatives (see *e.g.* B. **17**, 2384). For *syntheses*, cf. among others B. **20**, 154; **24**, 111, Ref. 575; A. **257**, 253; **262**, 89; **273**, 164.

2. **Pyrazine**, *aldine*, $C_4H_4N_2$ (colourless prisms, M. Pt. 55°, B. Pt. 115°), possesses a basic character (B. **26**, 721) and is the mother substance of the ketines, *e.g.* **Ketine** or *dimethyl-pyrazine*, $C_4H_2(CH_3)_2N_2$, which is obtained by the reduction of isonitroso-acetone or the condensation of amido-acetone (p. 157; B. **19**, 2524; **21**, 19).

"*Piperazine*" is formed by the addition of six hydrogen atoms to pyrazine. It is identical with diethylene-diamine (p. 210), and is employed in cases of gout and stone diseases on account of its solvent action on uric acid.

3. **Pyrimidine**, *miazine*. From this (unknown) mother substance there are derived the so-called **Cyan-methines**, which result from the polymerization of the nitriles, and a series of compounds which are produced by the action of aceto-acetic ester upon the amidines; also alloxan (p. 303). Cf. *E. v. Meyer*, J. pr. Ch. **39**, 188, 262; *Pinner*, B. **18**, 759, 2845; **23**, 3820.

A similar hexagon ring to that of pyrimidine, but with three symmetrically distributed nitrogen atoms, appears to form the basis of certain:

4. **Tricyanides**, *e.g.* *Cyaphenine*, $C_3N_3.(C_6H_5)_3$, which is formed from benzo-nitrile, benzoyl chloride, and sal-ammoniac in presence of chloride of aluminium (B. **25**, 2263; cf. also the cyanogen compounds).

5. **Morpholine**, C_4H_9NO. A methyl derivative of this base, **Methylmorpholine**, $(CH_3)N\!\begin{smallmatrix}\diagup CH_2-CH_2 \diagdown \\ \diagdown CH_2-CH_2 \diagup\end{smallmatrix}\!O$, results upon methylating dioxyethylamine, $NH\!\begin{smallmatrix}\diagup CH_2-CH_2.OH \\ \diagdown CH_2-CH_2.OH\end{smallmatrix}$ (p. 211), and subsequently heating with hydrochloric acid and alkali in succession (*i.e.* abstracting the elements of water indirectly). It is a liquid base (B. Pt. 117°) which resembles methylpiperidine both physically and chemically. It is readily soluble in water (*Knorr*, B. **22**, 2081). Morpholine appears to be the mother substance of morphine.

XXXIV. THE QUINOLINE AND ACRIDINE GROUPS; AZINES.

A. Quinoline Group, $C_nH_{2n-11}N$.

The quinoline group comprises quinoline, its substitution products, homologues, carboxylic acids, etc., all of which remind one of the corresponding compounds of the pyridine group in their behaviour (cf. p. 517 *et seq.*).

Quinoline stands to pyridine as naphthalene does to benzene.

Formation. 1. By the dry distillation of nitrogenous organic substances, and from alkaloids as given at p. 520. Cinchonine yields quinoline itself when heated with potash (*Gerhardt*, 1842), and quinine gives methoxy-quinoline (p. 535).

2. Quinoline is produced when aniline is heated with glycerine and sulphuric acid in presence of nitro-benzene (*Skraup*, B. 14, 1002; Monatsh. f. Chemie, I. 316; II. 141):

$$C_6H_4\begin{cases}H\\NH_2\end{cases} + \begin{matrix}CH_2(OH)-CH(OH)\\ \quad CH_2(OH)\end{matrix} + O = C_6H_4\begin{cases}CH=CH\\N=CH\end{cases} + 4H_2O.$$

Aniline. Glycerine. Quinoline.

The nitro-benzene simply acts as an oxidizing agent; the formation of acroleïn as intermediate product is to be assumed here, the latter combining in the first instance with aniline to acroleïn-aniline. The homologues and analogues of aniline yield homologues and analogues of quinoline by corresponding reactions; when naphthylamine is used, the more complicated naphtho-quinolines result (see below).

3. Quinoline is formed by the separation of the elements of water from *o*-amido-cinnamic aldehyde (*Baeyer* and *Drewson*, B. 16, 2207):

$$C_6H_4\begin{cases}CH=CH-CHO\\NH_2\end{cases} = C_6H_4\begin{cases}CH=CH\\N=CH\end{cases} + H_2O.$$

Carbostyril (α-oxy-quinoline) results in an analogous manner from *o*-amido-cinnamic acid (*Baeyer*):

$$C_6H_4\begin{cases}CH=CH\\NH_2CO.OH\end{cases} = C_6H_4\begin{cases}CH=CH\\N=C.(OH)\end{cases} + H_2O.$$

Of historical interest is a partly analogous synthesis of quinoline by the action of phosphorus pentachloride upon hydro-carbostyril (p. 453), and reduction of the resulting dichloro-quinoline, $C_9H_5NCl_2$, by means of hydriodic acid (*Baeyer*, B. 12, 1320).

4. When aniline is heated with aldehyde (para-aldehyde) and hydrochloric acid, α-methyl-quinoline (quinaldine) is obtained (*Doebner* and *v. Miller*):

$$C_6H_5.NH_2 + 2C_2H_4O + O = C_{10}H_9N + 3H_2O.$$

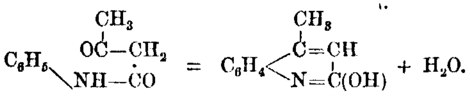
In this reaction ethylidene-aniline is formed as intermediate product (B. 24, 1720; 25, 2072):

$$C_6H_4\begin{cases}H\\NH_2\end{cases} + \begin{matrix}OCH-CH_3\\ \quad OCH-CH_3\end{matrix} + O = C_6H_4\begin{cases}CH=CH\\N=C(CH_3)\end{cases} + 3H_2O.$$

Aniline. Quinaldine.

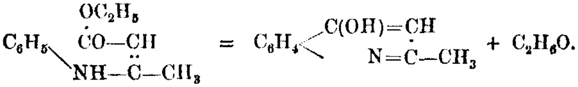
Here, again, various other primary aromatic amines may be used instead of aniline; and other aldehydes (B. **18**, 3361) or ketones (*e.g.* B. **19**, 1394) instead of para-aldehyde.

5. Aniline and aceto-acetic acid combine together at temperatures above 110° to aceto-acetanilide, $CH_3—CO—CH_2—CO.NH.C_6H_5$, from which γ-methyl-α-oxyquinoline ("methyl-carbostyril" or "α-oxy-γ-lepidine") results on the elimination of water (*Knorr*, A. **236**, 75):

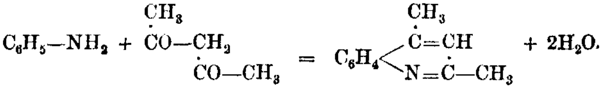


Aceto-acetanilide. γ-Methyl-carbostyril.

Aniline can also react with aceto-acetic ether (under 100°), with the formation of β-**Phenyl-amido-crotonic ether**, $C_6H_5—NH—C(CH_3)=CH—CO_2C_2H_5$, which yields γ-oxy-quinaldine when heated (*Conrad* and *Limpach*, B. **20**, 944):



Analogously to aceto-acetic ether (which is the ether of a β-ketonic acid), the β-diketones likewise condense with aniline; further, also, mixtures of ketones and aldehydes, or mixtures of aldehydes which would yield β-diketones or β-ketonic aldehydes if condensed together (*C. Beyer*, B. **20**, 1767). With acetyl-acetone we obtain (*e.g.*) α-γ-dimethyl-quinoline:

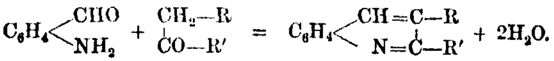


These reactions are nearly allied to those already spoken of under 4.

6. *o*-Amido-benzaldehyde undergoes condensation with aldehydes and ketones under the influence of dilute caustic soda solution, with the formation of quinoline derivatives (*Friedländer*, B. **15**, 2574; **16**, 1833; 25, 1752). With aldehyde quinoline itself results, and with acetone quinaldine:

$$C_6H_4(NH_2).CHO + C_3H_6O = C_{10}H_9N + 2H_2O;$$

or, generally:



Acetophenone, aceto-acetic ether, malonic ether, di-ketones, etc. also react in a similar way.

7. **Quinoline is produced when the vapour of allyl-aniline is led over heated oxide of lead (*Königs*);**

8. Also by oxidizing acridine to acridinic acid, $C_9H_5N(CO_2H)_2$ (p. 537), and eliminating the carboxyls.

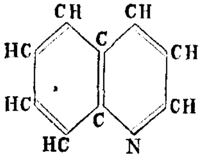
9. Derivatives of dihydro-quinoline are formed by the action of methyl iodide, etc. upon indoles (*E. Fischer* and *Steche*, A. **242**, 348).

10. For further syntheses see B. **18**, 632, 1460, 2632, 2975.

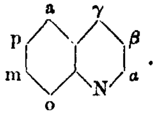
Constitution. The above modes of formation (especially 3 and 6) show that quinoline is an ortho-di-derivative of benzene, and that it contains its nitrogen linked directly to the benzene nucleus; they also show that the three C-atoms, which enter the complex, form a new hexagon (*pyridine*) ring with this nitrogen and with two carbon atoms of the benzene ring. The latter point also follows from the oxidation of quinoline to pyridine-dicarboxylic acid (*Hoogewerff* and *van Dorp*):

$$\underset{\text{Quinoline.}}{C_6H_4\left\langle\begin{array}{l}CH=CH\\ \;\;N=CH\end{array}\right.} + O_9 = \underset{\text{Quinolinic acid.}}{\begin{array}{l}CO_2H\;\;\;C-CH=CH\\ CO_2H-C-\;N=CH\end{array}} + 2CO_2 + H_2O.$$

We have thus the following constitutional formula:



or



The second of these two modes of writing the formula possesses this advantage over the first that it is independent of special assumptions with regard to the mode in which each fourth carbon- or third nitrogen-affinity is taken up. One may also assume here a mode of linking corresponding to that of *Claus's* benzene formula (cf. pp. 348 and 523).

Quinoline is thus constituted in a manner perfectly analogous to naphthalene, and may be looked upon as being derived from the latter by the exchange of CH for N, or by the "condensation" of a pyridine and a benzene nucleus.

When quinoline derivatives are oxidized, the benzene residue usually proves itself to be less stable than the pyridine one. This is shown in the case of quinoline itself, the benzene nucleus being destroyed upon its oxidation to pyridine-dicarboxylic acid (p. 527), a-Methyl-quinoline gives, on the other hand, acetyl-o-amido-benzoic acid when oxidized:

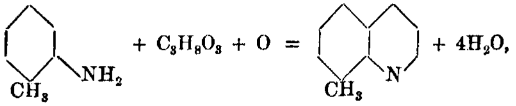
$$C_6H_4\left\langle\begin{matrix}CH=CH\\ N-\dot{C}.CH_3\end{matrix}\right. + O_5 = C_6H_4\left\langle\begin{matrix}CO.OH\\ NH-CO.CH_3\end{matrix}\right. + CO_2.$$

For laws governing the oxidation of quinoline derivatives, see *W. v. Miller*, B. **23**, 2252; **24**, 1900.

The pyridine nucleus of quinoline takes up hydrogen more readily than the benzene one; thus quinoline is easily converted (even by tin and hydrochloric acid) into tetrahydro-quinoline, although it can be reduced further only with difficulty (up to the deca-hydride).

The three H-atoms of the pyridine nucleus, counting from the N, are designated as α-, β and γ-, and the four H-atoms of the benzene nucleus as *o*-, *m*-, *p*- and *a*- (ana-) hydrogen atoms; or the former as Py-1, 2, and 3, and the latter as B-1, -2, -3 and 4 atoms (*Baeyer*, B. **17**, 960). Since no one of these H-atoms is linked symmetrically to another, seven mono-derivatives of quinoline are in each case theoretically possible. As a matter of fact all seven quinoline-monocarboxylic acids have been prepared.

The position of the substituents follows: (*a*) from the nature of the products which result upon oxidation, *e.g.* B-quinoline-carboxylic acid (*i.e.* one whose carboxyl is linked to the benzene nucleus) yields a pyridine-dicarboxylic acid, while a Py-quinoline-carboxylic acid (whose carboxyl is linked to the pyridine nucleus) yields a pyridine-tricarboxylic acid; (*b*) from the synthesis of the compound in question. The methyl-quinoline, for instance, which results from *o*-toluidine by the *Skraup* synthesis must be a B-1-compound:



whilst *m*-toluidine must yield a B-2- or B-4-, and *p*-toluidine a B-3-methyl-quinoline (a "tolu-quinoline").

Quinoline.

Quinoline, *leucoline*, C_9H_7N (*Runge*, 1834), is also found in Idrian "Stupp" fat (see p. 516). It is a colourless strongly refracting liquid of a peculiar and very characteristic odour; B. Pt. 236°. Quinoline is a monatomic base. It forms a difficultly soluble bichromate, $(C_9H_7N)_2, Cr_2O_7H_2$. Is used as an antifebrile.

The quaternary quinoline-ammonium bases show many peculiarities, which are possibly explicable on the assumption of a particular constitution (cf. *e.g. Roser*, A. **272**, 221).

Nascent hydrogen transforms it first into **Dihydro-quinoline**, C_9H_9N (*M. Pt.* 161°), and then into **Tetrahydro-quinoline**, $C_9H_{11}N$,

$$= C_6H_4 \langle \begin{matrix} CH_2-CH_2 \\ NH-CH_2 \end{matrix}$$ (liquid, B. Pt. 245°). Since both of these yield nitrosamines and can be alkylated, they are secondary bases. The tetrahydro-compound exerts a stronger antifebrile action than the mother substance, especially in the form of its ethyl-derivative, **Cairolin** (B. **16**, 739).

Quinoline decahydride, $C_9H_7.H_{10}.N$, results when quinoline is strongly hydrogenized. Crystals of a narcotic conine-like odour; M. Pt. 48°, B. Pt. 204°.

When quinoline is heated with sodium, a **Diquinolyline**, $C_9H_6N-C_9H_6N$, *analogous to diphenyl or dipyridine, is formed; it crystallizes in small* plates or needles. Quinoline also yields **Diquinoline**, $(C_9H_7N)_2$ (yellow needles), by polymerizing.

Halogen derivatives of quinoline and nitro-quinolines have been prepared by the *Skraup* reaction, etc.; and, from the reduction of the latter, amido-quinolines, $C_9H_6N(NH_2)$. The quinoline-sulphonic acids yield cyano-quinolines when heated with potassium cyanide, and oxy-quinolines when fused with potash. Certain of the last-named compounds likewise result from the amido-phenols by the *Skraup* reaction, these containing the hydroxyl in the benzene nucleus. *p*-**Methoxy-quinoline**, $C_9H_6N(O.CH_3)$, is the anisol of the quinoline series and resembles quinoline closely. For *its formation from quinine, see p. 531; it is also formed from p-anisidine* (*Skraup*). Its tetrahydro-compound, **Thalline**, $C_9H_{10}N(O.CH_3)$, is an anti-pyretic.

α-Oxy-quinoline, *carbostyril*, $C_6H_4(C_3H_2N.OH)$, is a quinoline hydroxylated in the pyridine nucleus (see p. 531, mode of formation 3). It crystallizes in white needles and is soluble in alkali, from which it is again thrown down by carbonic acid; M. Pt. 198–199°. Its constitution follows from its formation from *o*-amido-cinnamic acid (p. 531).

Homologues of Quinoline; condensed Quinolines.

Quinaldine, *α-methyl-quinoline*, $C_{10}H_9N$, is contained in coal tar. It is a colourless liquid of quinoline odour, which boils at 246°, and whose oxidation yields either a benzene or a quinoline derivative, according to the nature of the oxidizing agent (see p. 533).

The hydrogen of the methyl group readily enters into reaction; quinaldine reacts with phthalic anhydride to produce a beautiful yellow dye, **Quinoline-yellow**, $C_{10}H_7N(CO)_2C_6H_4$ (B. **16**, 2602). In presence of quinoline quinaldine is transformed into the (unstable) blue dyes, the **Cyanines**, when alkylated and treated with caustic potash.

γ-Methyl-quinoline, *γ-lepidine*, *cincho-lepidine*, $C_9H_6N(CH_3)$, is obtained by distilling cinchonine with oxide of lead; B. Pt. 264°.

The methyl-quinolines are isomeric with the naphthylamines. The homologues of quinoline which have been isolated from coal tar and bone oil are known as **Lepidine** or **Iridoline**, $C_{10}H_9N$, **Cryptidine**, $C_{11}H_{11}N$, etc.

Tetramethyl-quinoline, M. Pt. 64°, B. Pt. 284° (B. **19**, 1394).

Phenyl-quinoline, $C_9H_6N—C_6H_5$. Py-3-phenyl-quinoline,

$C_6H_4<\begin{matrix}C(C_6H_5)=CH\\ N=CH\end{matrix}$, is to be regarded as the mother substance of the cinchona alkaloids (*Königs* and *Nef*, B. **19**, 2427). *Formation*, see B. **18**, 2406.

Flavaniline, $C_{16}H_{14}N_2$, a beautiful yellow dye, which results upon heating acetanilide with zinc chloride, is an α-amido-phenyl-γ-methyl-quinoline (B. **15**, 1500).

Naphtho-quinolines, $C_{13}H_9N$. These compounds (solid bases), which are derived from phenanthrene by the exchange of CH for N, are obtained by subjecting the two naphthylamines to the *Skraup* reaction. They are isomeric with acridine (p. 537).

Anthra-quinoline, $C_{17}H_{13}N$, is formed in an analogous manner from anthramine (p. 511). It crystallizes in colourless plates and is the mother substance of alizarin blue (p. 514).

Quinoline-carboxylic Acids.

All the seven mono-carboxylic acids of quinoline, which are possible according to theory, are known. Quinoline-benz-carboxylic acids are those which contain the carboxyl group in the benzene nucleus.

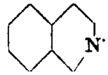
Cinchoninic acid, $C_9H_6N(CO_2H)$, which results from the oxidation of cinchonine by permanganate of potash and crystallizes in needles or prisms, M. Pt. 254°, is γ-quinoline-carboxylic acid. From it is derived

Quininic acid, $C_9H_5N(\overset{p}{O}CH_3).\overset{\gamma}{C}O_2H$, which is obtained by oxidizing quinine with chromic acid; it forms yellow prisms, M. Pt. 280°.

α-β-Quinoline-dicarboxylic acid or *acridinic acid*, results from the oxidation of acridine.

Bases related to Quinoline.

Iso-quinoline, an isomer of quinoline, occurs along with the latter in coal tar (B. **18**, Ref. 384). It is a solid; M. Pt. 23°, B. Pt. about 240°. Since oxidation converts it into cinchomeronic acid (β-γ-Py-dicarboxylic

acid) on the one hand and phthalic acid on the other, it possesses the constitution:  *Synthesis*:—That from β-naphtho-quinone (B. **25**, 1138, 1493) is of especial interest, since it demonstrates the close relations between the different ring systems; see also B. **19**, 2354; **21**, 2299; **25**, 733.

Bases related to quinoline, which contain in the molecule two atoms of N instead of (CH) and N, and which have the formula $C_6H_4(C_2H_2N_2)$, have recently been prepared in considerable number, either themselves or in the form of derivatives; among these are the *Cinnoline-*, *Quinazole-*, etc. compounds and the *Quinoxalines* (B. **16**, 677; **17**, 318, 724; **19**, 1604; **20**, Ref. 255, 630; **21**, Ref. 571; **22**, 2683).

Quinoxaline or *quinazine*, $C_6H_4\!<\!\begin{matrix}N=CH\\ |\\ N=CH\end{matrix}$, results from the action of glyoxal upon *o*-phenylamine-diamine. In a similar manner *o*-diamines combine with aldehyde acids, di-ketones, ketonic acids, etc., if these latter contain two neighbouring CO-groups (see *e.g.* B. **25**, 604, 2416; **24**, 1870; also under phenazine, p. 539). Quinoxaline is a chromogene.

B. The Acridine Group, $C_nH_{2n-17}N$.

Acridine, $C_{13}H_9N$ (*Graebe* and *Caro*), is a base crystallizing in colourless needles and capable of being sublimed, which is present in the crude anthracene of coal tar, and also in crude diphenylamine. It is characterized by an intensely irritating action upon the epidermis and the mucous membrane, and also by the greenish-blue fluorescence shown by dilute solutions of its salts.

It is prepared synthetically by heating diphenylamine and formic acid, or formyl-diphenylamine, $(C_6H_5)_2N.CHO$, with zinc chloride (*Bernthsen*, A. **224**, 1), and is also obtained when the vapour of *o*-tolyl-aniline is passed through a red-hot tube.* Oxidation converts it into α-β-quinoline-dicarboxylic acid (p. 536); its formation and constitution are thus shown by the following equation:

$$\underset{\text{Formyl-diphenylamine.}}{C_6H_5\overset{CHO}{\underset{N}{\diagdown\!\!\diagup}}C_6H_5} = \underset{\text{Acridine.}}{C_6H_4\!<\!\begin{matrix}CH\\ N\end{matrix}\!>\!C_6H_4} + H_2O.$$

It consequently appears as an anthracene in which the middle group CH is replaced by N. Acridine is a tertiary base.

Methyl- and Butyl-acridines, Phenyl-acridine, $C_6H_4\!<\!\begin{matrix}C(R)\\ N\end{matrix}\!>\!C_6H_4$, **and Naphtho-acridines** (*i.e.* acridines which contain $C_{10}H_6$ instead of C_6H_4), **have all been prepared synthetically in an analogous manner.**

* Cf. B. **25**, 1733.

Methyl-acridine can be oxidized indirectly to **Acridyl aldehyde,** $C_{13}H_8N—CHO$, and **Acridine-carboxylic acid,** $C_{13}H_8N—CO_2H$ (B. **20**, 1541). The latter compound crystallizes in yellow needles and is at the same time base and acid.

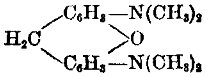
Diamido-dimethyl-acridine, *acridine yellow*, $C_{13}H_5(CH_3)_2N(NH_2)_2$, a yellow basic dye, results on condensing formic aldehyde with *m*-toluylene-diamine, splitting off ammonia, and oxidizing the leuco-base produced.

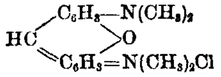
The **Chrysaniline** or *phosphin* of commerce, a beautiful yellow dye, is *diamido-phenyl-acridine*, $C_{19}H_{11}N(NH_2)_2$, since it yields phenyl-acridine when its diazo-compound is boiled with alcohol.

Acridine is therefore, like anthracene, a chromogene (see p. 32).

Appendix. Diphenylene-methane Oxide Group.

The oxygenated compound **Diphenylene-methane oxide,** $C_6H_4\!<\!{}^{CH_2}_{O}\!>\!C_6H_4$, which can be prepared synthetically and also by distilling euxanthone over zinc dust, corresponds in composition to hydro-acridine, $C_6H_4\!<\!{}^{CH_2}_{NH}\!>\!C_6H_4$. It crystallizes in plates, M. Pt. 98·5°. It is on the one hand the mother substance of xanthone (p. 483) and its derivative euxanthone, and on the other hand of the rhodamines and fluoresceïns. Its **Tetramethyl-diamido-** derivative results from the condensation of formic aldehyde with dimethyl-*m*-amido-phenol to tetramethyl-diamido-dioxy-diphenyl-methane and subsequent intramolecular separation of water (ring-formation), and is the leuco-compound of **Formo-rhodamine** or *pyronine*, $C_{17}H_{19}N_2OCl$, into which it passes upon oxidation and production of quinoid linking, thus:


Leuco-compound.


Formo-rhodamine hydrochloride.

Benzo-, succino-, and phthalo-rhodamines (p. 495) are also derived from this dye. Fluorane (p. 495), and its derivatives fluoresceïn, etc., likewise belong to the same group.

C. Azines, Oxazines, and Thiazines.

In anthracene and hydro-anthracene two benzene nuclei are joined together by two (CH)- and (CH_2)-groups respectively, in acridine by one (CH)-group and one nitrogen atom in an analogous manner, and in hydro-acridine by one (CH_2)- and one (NH_2)-group, these being always in the *ortho*-position to one another. A similar junction of two benzene nuclei can

be brought about by two nitrogen atoms or imido-groups (likewise in the *o*-position to one another), thus:

$$C_6H_4<\begin{matrix}N\\N\end{matrix}>C_6H_4. \qquad C_6H_4<\begin{matrix}NH\\NH\end{matrix}>C_6H_4.$$

(I.) Phenazine. (II.) Hydro-phenazine.

Also by an imido-group and an oxygen or sulphur atom, thus:

$$C_6H_4<\begin{matrix}NH\\O\end{matrix}>C_6H_4. \qquad C_6H_4<\begin{matrix}NH\\S\end{matrix}>C_6H_4.$$

(III.) Phenoxazine. (IV.) Phenthiazine (thio-diphenylamine).

In these compounds the benzene nuclei may be replaced by those of naphthalene, with the formation (*e.g.*) of—

$$C_{10}H_6<\begin{matrix}N\\N\end{matrix}>C_{10}H_6 \qquad C_{10}H_6<\begin{matrix}NH\\O\end{matrix}>C_6H_4, \text{ etc.}$$

Naphthazine. Naphtho-phenoxazine.

The compounds (II.) to (IV.) of the type of hydro-anthracene pass into the leuco-compounds of dyes upon the entrance of amido- (alkyl-amido-) or of hydroxyl groups holding the *para-position to the nitrogen. The colours themselves are then* obtained from these by oxidation (*i.e.* abstraction of H_2), so that the dyes derived from (II.) appear likewise as amido- (or oxy-) phenazines. In this way the (mono-amidated) eurhodines and the (di-amidated) toluylene red dyes are derived from phenazine and hydro-phenazine, and also the safranines and indulines; Nile blue springs from naphtho-phenoxazine; and the thionine dyes from phen-thiazine.

1. The Azines.

Phenazine, or *azo-phenylene*, $C_{12}H_8N_2$, results from the distillation of barium azo-benzoate, upon leading the vapour of aniline through red-hot tubes, and by the oxidation of its hydro-compound (see below). It crystallizes in beautiful long bright yellow needles, M. Pt. 171°, which can be readily sublimed, is only sparingly soluble in alcohol, but easily in ether, and soluble in concentrated sulphuric acid with a red colour; the alcoholic solution yields a green precipitate on the addition of stannous chloride. When reduced with sulphide of ammonium it goes into a colourless hydro-compound, **Hydro-phenazine**, $C_6H_4<\begin{matrix}NH\\NH\end{matrix}>C_6H_4$ (readily oxidizable plates).

This latter is also formed synthetically by heating pyrocatechin with *o*-phenylene-diamine (B. **19**, 2206):

$$C_6H_4<{OH \atop OH} + {NH_2 \atop NH_2}>C_6H_4 = C_6H_4<{NH \atop NH}>C_6H_4 + 2H_2O.$$

In accordance with the formula $C_6H_4<{N \atop N}>C_6H_4$, phenazine may also be regarded as a derivative of (the unknown) *ortho*-Benzo-quinone, $C_6H_4<{O \atop O}$, in which the two oxygen atoms are linked to neighbouring carbon atoms of the ring (cf. Quinone, p. 427). Phenazine is also closely related to quinoxaline (p. 537).

Naphtho-phenazine, $C_{10}H_6<N_2>C_6H_4$, results from the action of acids upon the azo-dyes derived from phenyl-β-naphthylamine (B. **20**, 571). It forms lemon-yellow crystals which can be sublimed.

Naphtho-tolazine, $C_{10}H_6<N_2>C_6H_3(CH_3)$, is very similar.

For isomeric **Naphthazines**, $C_{20}H_{12}N_2$, cf. A. **237**, 327; **272**, 307; B. **26**, 183.

Eurhodine, *amido-naphtho-tolazine*, $H_2N.C_{10}H_5<N_2>C_6H_3(CH_3)$, is obtained by warming α-naphthylamine with *o*-amido-azo-toluene dissolved in phenol. Lustrous golden crystals, soluble in ether with a yellowish-green fluorescence and in dilute hydrochloric acid to a red solution (B. **19**, 441; **21**, 2418; **24**, 1337). When heated with acid it is converted into the basic and at the same time phenolic compound:

Eurhodol, $HO.C_{10}H_5<N_2>C_6H_3(CH_3)$ (yellow crystals); cf. B. **24**, 1337.

o-**Diamido-phenazine**, $C_{12}H_6N_2(NH_2)_2$, results from the oxidation of *o*-phenylene-diamine with ferric chloride (B. **22**, 355); and a hetero-nucleal isomer, analogous to toluylene red, from a mixture of *m*- and *p*-phenylene diamines (B. **23**, 1852).

Toluylene red, $C_{15}H_{16}N_4$ (*Witt*). When *p*-amido-dimethyl-aniline is oxidized in the cold along with *m*-toluylene-diamine, the beautiful blue compound Toluylene blue, an indamine (p. 389), results, which gives up hydrogen and goes into toluylene red when boiled:

$$\underset{\text{Amido-dimethyl-aniline.}}{(CH_3)_2N{-}C_6H_4{-}NH_2} + \underset{\text{Toluylene-diamine.}}{NH_2{-}C_6H_3(CH_3)(NH_2)} + O_2$$

$$= \underset{\text{Toluylene red.}}{(CH_3)_2N{-}C_6H_3<{N \atop N}>C_6H_2(CH_3){-}NH_2} + 3H_2O.$$

Other similar compounds can be prepared in an analogous manner. The simplest toluylene red, which results from *p*-phenylene-diamine and *m*-toluylene-diamine and which contains NH_2 in place of $N(CH_3)_2$, yields **Methyl-phenazine**, $C_6H_4\{N_2\}C_6H_3(CH_3)$, when diazotized.

Toluylene red is used on the technical scale as "Neutral red."

For **Tri-** and **Tetramido-phenazine**, cf. B. **22**, 3039.

Safranines.

The **Safranines** are related to toluylene red. They are produced by oxidizing an aqueous solution of a mixture of the sulphates of *p*-phenylene-diamine (1 mol.) with a primary monamine (1 mol.) and a second monamine in which the *p*-position is unoccupied (1 mol.). The simplest safranine is **Pheno-safranine,** $C_{18}H_{15}N_4Cl$ [from $C_6H_4(NH_2)_2 + 2C_6H_5.NH_2$], while the ordinary safranine of commerce consists principally of **Tolu-safranine,** $C_{21}H_{10}N_4$, HCl [from $C_6H_3(CH_3)(NH_2)_2$ (1 : 2 : 4) and $2C_6H_4(CH_3)NH_2$]. See B. **16**, 472, etc. The requisite mixture of mono- and diamines is attained in practical working by the reduction of amido-azo-compounds (see p. 404).

The safranines are beautiful crystalline compounds of a metallic green lustre, readily soluble in water, which dye yellowish-red, red and violet. The solution in concentrated sulphuric acid is green, becoming blue, violet, and finally red on dilution with water. Reduction gives rise to leuco-compounds, which are diamido-compounds of the as yet unknown substance $C_6H_4\left<{NH \atop N(C_6H_5)}\right>C_6H_4$ (B. **19**, 2690, 3017, 3121, etc.).

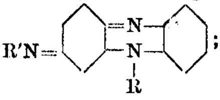
The safranines are therefore probably diamido-compounds of a still unknown "azonium" base, $C_6H_4\left<{N \atop {N(C_6H_5) \atop OH}}\right>C_6H_4$.

Mauveïne, *phenyl-safranine,* $C_{21}H_{20}(C_6H_5)N_4Cl$, was the first aniline dye to be prepared on the technical scale (by *Perkin* in 1856, from crude aniline, bichromate of potash and sulphuric acid).

Magdala red, $C_{30}H_{21}N_4Cl$, is the safranine of the naphthalene series.

Indulines.

The dyes of this group contain the peculiar *induline ring:*



; this appears on the one hand as a derivative of a pseudo-form of phenazine (the latter base being obtained *e.g.* from benzinduline), while on the other it is derived from (*para*)-quinone, seeing that two atoms or groups in the *para*-position to one another are linked to one benzene ring by double bonds (*i.e.* in "quinoid" linkage).

The benzindulines are direct derivatives of this induline ring, while the rosindulines and naphthindulines are referable in the same way to correspondingly modified naphtho-phenazines and naphthazines respectively.

The indulines are violet-blue to grey-blue dyes which result upon heating amido-azo-benzene with the aniline hydrochlorides, and sulphurating the product so obtained. *Para*-quinone-anilides are formed here as intermediate products, *e.g.* **Azo-phenine** or *dianilido-quinone-dianile* (p. 430, B. **21**, 676; *Witt*, B. **20**, 2659); the formation of these from the amido-azo-compounds is explicable from the latter acting to a certain extent as oxidizing agents, and also at the same time as the source of the *para*-diamines which result by their reduction (*O. Fischer* and *Hepp*, B. **25**, 2731; cf. also p. 403).

Phenyl-induline, $C_{18}H_{13}N_3$, $= HN{=}C_6H_3{<}{}^{N}_{N(C_6H_5)}{>}C_6H_4$, is the simplest benzinduline. M. Pt. 125°. It yields reddish-violet salts which are soluble in water. The more complex and bluer indulines, $C_{24}H_{18}N_4$, $C_{36}H_{27}N_5$, etc., whose sulpho-salts constitute the **Fast Blue**, etc. of commerce, are derived from phenyl-induline by the further entrance of phenyl- and amido-phenyl groups into the molecule.

When phenyl-induline is warmed with hydrochloric acid, **Benzene-indone**, $C_{18}H_{12}N_2O$ (in which the imido-group of the phenyl-induline is replaced by oxygen) is obtained among other products. It crystallizes in small plates with a metallic lustre, and yields phenazine when distilled with zinc dust.

Phenyl-rosinduline, $C_{28}H_{19}N_3$, an induline of the naphtho-phenazine series, results upon heating (*e.g.*) benzene-azo-α-naphthylamine with aniline and aniline hydrochloride. Its disulpho-acid is the valuable orceïn-red dye, **Azo-carmine**. For the literature on this subject, see *O. Fischer* and *Hepp*, B. **23**, 838; A. **256**; **262**; **266**; **272**, 306.

Aniline black ($C_{30}H_{27}N_5$?), obtained by acting upon aniline with (*e.g.*) potassium chloride in presence of copper or vanadium salts, is produced directly upon the fibre; it is a dark green amorphous powder, insoluble in most menstrua.

2. Oxazines.

Phenoxazine, $C_6H_4{<}{}^{NH}_{O}{>}C_6H_4$, is obtained by heating pyrocatechin with *o*-amido-phenol; sublimable plates.

Nile Blue, $HN{=}C_{10}H_5{<}{}^{N}_{O}{>}C_6H_3{-}N(C_2H_5)_2$, HCl, whose leuco-base is a di-ethylated diamido-naphtho-phenoxazine, results upon converting diethyl-*m*-amido-phenol into its nitroso-compound, and heating the latter with α-naphthylamine. It is a magnificent greenish-blue basic dye.

Gallo-cyanine, $C_{15}H_{13}N_2O_5Cl$, a blue-violet dye which, like alizarin, requires a mordant, is prepared by the action of nitroso-dimethyl-aniline upon gallic acid

3. Thiazines (Thionine dyes).

Phen-thiazine, *thio-diphenylamine,* $C_6H_4<^{NH}_{S}>C_6H_4$. Cf. p. 389. When nitrated and then reduced, this compound yields:

Diamido-thio-diphenylamine, *leuco-thionine,* $C_{12}H_7NS(NH_2)_2$, the leuco-compound of the less hydrogenized:

Thionine, $C_{12}H_9N_3S$, whose hydrochloride is **Lauth's Violet.**

$$\textbf{Methylene Blue, } C_{16}H_{18}N_3SCl, = N\begin{matrix} \diagup C_6H_3-N(CH_3)_2 \\ \quad\quad >S \\ \diagdown C_6H_3=N(CH_3)_2Cl \end{matrix}$$

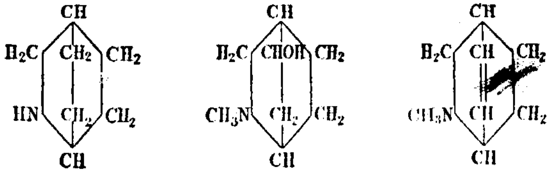
(*Caro,* 1876), a blue dye which is particularly valuable for cotton, results from the action of ferric chloride upon amido-dimethyl-aniline, in presence of sulphuretted hydrogen; also by oxidizing the latter base in presence of thio-sulphuric acid to **Amido-dimethyl-aniline-thiosulphonic acid,** $C_6H_3(N[CH_3]_2)(NH_2)(S.SO_3H)$, joining this (by oxidation) with dimethyl-aniline to the corresponding indamine, and boiling the latter with chloride of zinc. Cf. *Bernthsen,* A. **230,** 73; **251,** 1.

XXXV. ALKALOIDS OF COMPLEX OR UNKNOWN CONSTITUTION.

Some of the alkaloids which occur in nature are free from oxygen, liquid, and volatile without decomposition; while others contain oxygen, are (usually) solid and crystalline, and are not volatile without decomposition (strychnine volatilizes in a vacuum). They are precipitated by certain reagents such as tannic acid, phospho-molybdic acid, platinic chloride, the double iodide of mercury and potassium, potassic iodide, etc. Many of them give intense colour reactions with nitric acid, chlorine water, concentrated sulphuric acid, etc.

A. The Tropine Group.

The degradation products of the important alkaloids atropine and cocaine probably contain a peculiar and but slightly stable *combination of a piperidine- with a hexahydro-benzene ring,* in which four carbon atoms are common to both systems (*Merling,* 1891):



Hypothetical mother substance. **Tropine.** **Tropidine.**

These formulæ explain in an especial degree how the formation of the most varied decomposition-products is brought about, in that the hexa-hydro-benzene ring is sometimes broken and derivatives of hydro-pyridine ensue, while in other cases the piperidine ring is split up and hydrogenized benzene derivatives result (see below; also B. **24**, 3108; **25**, 1391). The formula of tropine, given above, receives further support from a beautiful synthesis of that compound from dihydro-benzyl-dimethylamine (Chem. Ztg. for 1892, p. 319).

The above compounds were formerly held as derived from a tetrahydro-pyridine with a long side-chain, *e.g.* tropine was regarded as α-oxyethyl-n-methyl-tetrahydro-pyridine. But this latter compound (p. 528) has been synthetized and found to be quite different from tropine (*Lipp*, B. **25**, 2197).

Tropine, $C_8H_{15}NO$, is obtained by decomposing atropine by means of baryta water. It is a tertiary base crystallizing in plates; M. Pt. 62°, B. Pt. 220°. When it is oxidized with chromic acid, the hexa-methylene ring is broken and *Tropinic acid*, $C_5H_8N(CH_3)(CO_2H)_2$,—the dicarboxylic acid of a methylated piperidine in which the methyl group is attached to the nitrogen—is formed. Concentrated hydrochloric acid converts tropine into:

Tropidine, $C_8H_{13}N$, an oily base, B. Pt. 162°, which likewise results on the separation of carbon dioxide from anhydro-ecgonine.

Ecgonine, $C_9H_{15}NO_3$, = $C_8H_{14}NO.CO_2H$. White prisms; lævo-rotatory. Ecgonine is a carboxylic acid of tropine (*Einhorn*), and therefore an oxy-acid. As an alcohol it forms a benzoic ester and as an acid a methyl ester, from a mixture of which cocaïne can be synthetized (see below).

Anhydro-ecgonine, $C_9H_{13}NO_2$, stands in the same relation to ecgonine as tropidine does to tropine. When its dibromide is treated with soda the piperidine ring is broken up, with the production of dihydro-benzaldehyde (p. 435) and methylamine (*Einhorn*, B. **26**, 451).

Cocaïne, $C_{17}H_{21}NO_4$, is the active constituent of the coca leaf (Erythroxylon coca), and is well known for its property of deadening pain. Lævo-rotatory. Its hydrochloride crystallizes in white prisms.

Hydrochloric acid breaks it up into benzoic acid, ecgonine and methyl alcohol, and it may be conversely reproduced by benzoating ecgonine and then methylating the resulting benzoyl-ecgonine. Homologous cocaïnes have been prepared in a similar manner.

Several of the compounds of this group are known in different optically active modifications (B. **23**, 979; **25**, 927).

B. Opium Bases.

Opium (Papaver somniferum) contains:

1. **Morphine**, $C_{17}H_{19}NO_3$, = $C_{17}H_{17}NO(OH)_2$, a monatomic

and tertiary base. It crystallizes in small prisms ($+ H_2O$) of bitter taste, and is a valuable soporific.

When distilled with zinc dust it yields phenanthrene in addition to pyrrol, pyridine and quinoline, and it is also convertible into phenanthrene derivatives in another way (A. **222**, 235). It appears to be a derivative of morpholine (p. 530). For its *constitution*, cf. *Knorr*, B. **22**, 181, 1113; *Skraup*, Monats. f. Chemie, **10**, 101.

2. **Codeïne**, *methyl-morphine*, $C_{18}H_{21}NO_3$, can be prepared by methylating morphine.

3. **Thebaïne**, $C_{19}H_{21}NO_3$. 4. **Narceïne**, $C_{23}H_{29}NO_9$.

5. **Papaverine**, $C_{21}H_{21}NO_4$, and 6. **Berberine**, $C_{20}H_{17}NO_4$, are derivatives of iso-quinoline. For their *constitution*, see Monats. f. Chemie, **9**; B. **24**, Ref. 157.

7. **Narcotine**, $C_{22}H_{23}NO_7$, crystallizes in glancing prisms. It is decomposed by the action of water into **Meconine**, $C_{10}H_{10}O_4$ (cf. p. 467, the anhydride of meconinic acid), also present in opium, and **Cotarnine**, $C_{12}H_{13}NO_3$ (prisms, $+ H_2O$), which latter is convertible by bromine into dibromo-pyridine. Like papaverine it is a derivative of benzyl-isoquinoline. For *constitution*, see *Roser*, A. **254**, 351, 356.

C. Cinchona Bases.

Quinine barks (*i.e.* the Cinchona varieties) contain:

1. **Quinine**, $C_{20}H_{24}N_2O_2 + 3H_2O$, a diatomic base of intensely bitter taste and alkaline reaction, whose sulphate and chloride are universally used as febrifuges. It crystallizes in prisms or silky glancing needles; M. Pt. 177°. The quinine salts in dilute solution are characterized by a magnificent blue fluorescence.

As a base quinine is a tertiary diamine, but it contains in addition—as its reactions show—a hydroxyl and a methoxyl, and seems to be built up of two different ring-systems, in accordance with the following formula:—

$$(CH_3O).C_9H_5N—C_{10}H_{15}(OH)N.$$

The first of these represents the radicle of a *p*-methoxy-quinoline, this latter compound being obtained on fusing quinine with potash (p. 535). The second system probably possesses a ring similar to that of tropine, since it yields as decomposition-products sometimes a pyridine derivative (*e.g.* β-ethyl-pyridine on fusion with alkali), and sometimes benzene derivatives containing no nitrogen (*e.g.* a phenolic compound, $C_{10}H_{12}OH$, together with

ammonia, on successive treatment with phosphorus pentachloride, potash, and hydrobromic acid).

It yields quininic acid, $C_9H_5N(OCH_3)CO_2H$ (p. 536), and **Cincho-loiponic acid**, $C_{18}H_{13}NO_4$, upon oxidation; and **Apo-quinine**, $C_{19}H_{20}N_2(OH)_2$, when warmed with hydrochloric acid, methyl being separated. Cf. B. **14**, 1852; A. **204**, 90; *Skraup*, Monats. f. Chemie, **10**, 220; *Königs* and *Comstock*, B. **25**, 1539 (where a *résumé* of the literature on the subject is given); **26**, 713.

2. **Cinchonine**, $C_{19}H_{22}N_2O$, = $C_{19}H_{21}N_2(OH)$, is derived from quinine by the exchange of (OCH_3) for H. It forms white sublimable prisms or needles, is a weaker febrifuge than quinine, and yields cinchoninic acid upon oxidation and quinoline on fusion with potash.

3. **Conchinine**, $C_{20}H_{24}N_2O_2$, and 4. **Cinchonidine**, $C_{19}H_{22}N_2O$, are isomeric with quinine and cinchonine respectively, and milder in their action.

D. Strychnine Bases.

Strychnos nux vomica and certain other beans, etc. contain:

1. **Strychnine**, $C_{21}H_{22}N_2O_2$, and 2. **Brucine**, $C_{23}H_{26}N_2O_4$. The former, which is excessively poisonous (producing tetanic spasms) crystallizes in four-sided prisms and yields quinoline and indole when fused with potash, and β-picoline, etc., when distilled with lime. (For recent literature on this subject, see A. **264**, 33; **268**, 229.) Brucine (prisms) is converted into homologues of pyridine on fusion with potash.

E. Solanine Bases.

Atropine, Hyoscyamine and Hyoscine are three isomeric bases of the formula $C_{17}H_{23}NO_3$, which can be respectively prepared from Atropa Belladonna, Datura Stramonium and Hyoscyamus niger, and which are remarkable for their mydriatic action (power of dilating the pupil of the eye).

Atropine crystallizes in colourless prisms or needles, possesses an extremely bitter taste, and is broken up by baryta water into tropic acid and tropine, $C_8H_{15}NO$ (p. 544), being therefore the tropic ester of the latter. Tropic acid and tropine reunite again to form atropine when their dilute hydrochloric acid solutions are evaporated together.

When optically active (*d*- and *l*-) tropic acids are used, a dextro- and lævo-rotatory atropine result (B. **22**, 2590). And if, instead of tropic acid

itself, a homologue is employed, homologous bases, the "**Tropeïnes**" are obtained; thus mandelic acid yields **Homatropine**, $C_{16}H_{21}NO_3$, which exerts like atropine a mydriatic action, although a less lasting one (*Ladenburg*, A. **217**, 82).

Hyoscyamine (needles or plates, M. Pt. 109°) resembles atropine closely, and is readily transformed into the latter, *e.g.* under the influence of alcoholic potash (*Will*, B. **21**, 1725, 2777). Its components are very possibly *l*-tropic acid and *l*-tropine, in which case it would be stereo-isomeric with atropine (B. **22**, 2590).

Hyoscine, M. Pt. 55°, is likewise decomposed by baryta water into tropic acid and tropine (?), and is perhaps stereo-isomeric with the above compounds (B. **25**, 933, 2388; A. **271**, 100).

F.

Among other alkaloids may be mentioned:

Corydaline, $C_{22}H_{29}NO_4$, from Corydalis cava. Flat colourless prismatic crystals, M. Pt. 134·5°. Yields the hydriodide of a base, $C_{18}H_{21}NO_4$, with hydriodic acid, four methoxy-groups being split off, and *Corydalinic acid*, $C_{19}H_{21}NO_{12}$, when oxidized with permanganate (*Dobbie* and *Lauder*, Ch. Soc. J. for 1892, pp. 244, 605; 1894, p. 57).

Veratrine, $C_{22}H_{42}NO_9$, from Veratrum album.

Sinapine, $C_{16}H_{23}NO_5$ (from the seed of white mustard), is a derivative—not of pyridine—but of choline on the one hand and of gallic acid on the other.

Sparteïne, $C_{15}H_{26}N_2$ (in Spartium scoparium).

For the alkaloids produced by the decomposition of dead bodies, which are termed Ptomaïnes, see p. 563.

XXXVI. TERPENES AND CAMPHORS.

The terpenes are hydrocarbons of the formula $C_{10}H_{16}$ [or $(C_5H_8)_x$], some of which are nearly related to cymene (p. 364), and others to other benzene derivatives. The camphors, *e.g.* Japan Camphor, $C_{10}H_{16}O$, contain oxygen in addition, but are closely allied to the terpenes. Both classes of compounds are widely distributed in nature.

Ethereal oils. Many plants contain, especially in their blossoms and fruits, oily substances to which they owe their peculiar fragrance or odour, and which can be obtained from them *e.g.* by distillation with steam. These, which are termed ethereal oils, were formerly grouped together in a special class, but now they are recognized as being more or less heterogeneous; thus oil of bitter almonds is benzoic aldehyde, and Roman oil of cumin is a mixture of cymene and cumic aldehyde, etc. Many of these ethereal oils contain terpenes, *e.g.* oil of thyme consists of thymene (a terpene) together with cymene and thymol; in fact the terpenes are often among their chief constituents, as in the case of turpentine, citron, and orange oils, etc. We further meet in some with olefinic alcohols, aldehydes, or ketones (for instance *linalool* and *citral*) which are isomeric with certain varieties of camphor, and which readily allow of ring-formation, and thus pass into terpenes (see appendix, p. 558). Many oils deposit solid substances, the "stearoptenes," when exposed to cold, the liquid portions being termed "Elæoptenes." The camphor varieties resemble the ethereal oils in their occurrence and modes of preparation, but they are solid.

A. Terpenes.

(Cf. especially *O. Wallach*, B. **24**, 1525, where references to the literature on the subject are given; A. **268** *et seq.*; **272**, 99; *Baeyer*, B. **26**, 232, 820.)

The terpenes are widely distributed in the vegetable kingdom, especially in the Coniferæ (Pinus, Picea, Abies, etc.), in the varieties of Citrus, etc. The products which are isolated in the first instance from the individual plants, and which according to their source are designated terpene, citrene (from oil of citron), hesperidene (from oil of orange), thymene (from thyme), carvene (from oil of cumin), eucalyptene, olibene, etc., have for the most part the formula $C_{10}H_{16}$ and approximately equal boiling points (160°–190°); they are not, however chemical individuals but mixtures of isomeric compounds.

With the exception of camphene they are all liquid, but it is hardly

possible to separate them completely by fractional distillation (see table, p. 550, for boiling points). The terpenes can, however, be obtained chemically pure from crystalline derivatives. Quite recently, too, compounds belonging to this class have been synthetized (see below).

Many terpenes are nearly related to cymene, $C_{10}H_{14}$; thus oil of turpentine goes directly into cymene when heated with iodine, and it yields, like the *para*-dialkyl-benzenes, terephthalic acid, $C_6H_4(CO_2H)_2$, upon oxidation, etc. They are therefore to be regarded in part as di-hydrides of cymene, $C_{10}H_{14}.H_2$ (see p. 364). Some show a close relation to *o* xylene (see Cantharene), and others to *m*-xylene see Cineol). The terpenes are also capable of forming addition-compounds which frequently lead as far as to derivatives of $C_{10}H_{20}$, *i.e.* to compounds whose benzene nucleus is completely reduced. They unite with hydrochloric acid to di-hydrochlorides, $C_{10}H_{18}Cl_2$, or—in the case of the pinenes and camphenes—to mono-hydrochlorides, $C_{10}H_{17}Cl$, only. They often form with bromine characteristic tetrabromides, $C_{10}H_{16}Br_4$. They readily yield compounds with nitrosyl chloride, of the formula $C_{10}H_{16}.NOCl$, on treatment with ethyl nitrite, glacial acetic acid and hydrochloric acid. Lastly, two of the terpenes—terpinene and phellandrene—combine easily with nitrous acid to form "Nitrosites," $C_{10}H_{16}N_2O_3$.

The combination with bromine and with halogen hydride is readily effected in an acetic acid solution. When the solution of the halogen hydride addition-product in glacial acetic acid is heated with sodium acetate, the halogen acid is split off.

The nitroso-chlorides, which are solid compounds melting at about 100°, react readily with organic bases—*e.g.* piperidine, ethylamine, aniline, etc.—to produce other well-characterized bases, the *Nitrolamines*, $C_{10}H_{16}(NO)(NRR')$:

$$C_{10}H_{16}\lt{}^{NO}_{Cl} + NH_2R = C_{10}H_{16}\lt{}^{NO}_{NHR} + HCl.$$

Among those the nitrol-benzylamines (prepared from benzylamine) may be instanced as specially well suited for the recognition and characterization of the terpenes.

Many terpenes show a great tendency to pass into more stable isomers under certain conditions, *e.g.* when acted upon by acids. They also polymerize readily. When in solution in acetic anhydride or alcohol, they give (yellow) red or blue colour-reactions with concentrated sulphuric acid.

Optical behaviour of the terpenes. The behaviour of the terpenes with regard to polarized light is very interesting. They are almost all optically active, and most of them exist both in dextro- and in lævo-rotatory modifications. While no appreciable alteration in properties (with the exception of the resulting optical inactivity) is as a rule apparent upon mixing equivalent amounts of these modifications, there results, oddly enough, when dextro- and lævo-limonene are mixed together, a peculiar "racemic compound," inactive dipentene, the derivatives of which differ materially from those of its components in boiling point, in melting point, and in solubility.

The terpenes are divisible into three main groups:

(*a*) Those which are capable of combining with one molecule of halogen hydride only, provided they do not in the meantime change into isomers:—pinene and camphene;

(*b*) Those which can unite with two molecules of halogen hydride, but not with nitrous acid:—dipentene, sylvestrene and terpinolene;

(*c*) Those which form nitrosites with nitrous acid:—terpinene and phellandrene.

They differ further in the boiling points, melting points, and properties of the mono- and di-hydrochlorides, and of the bromine addition-products (mainly tetrabromides), etc.

Summary.

	M. Pt.	B. Pt.	Bromides, M. Pt.	Hydrochlorides, M. Pt.	Nitrites, M. Pt.
1. Pinene - -	Liq.	159°–160°	Br_2 : 170°	+ HCl : 125°	—
2. Camphene -	50°	160°–161°	—	„ : decomp.	—
3. Fenchene -	Liq.	158°–160°	Br_2 : liq.	„ : liq.	—
4. ± Limonene	Liq.	175°	Br_4 : 104°	+ 2HCl : 50°	—
4*a*. Dipentene -	„		„ 125°		—
5. Sylvestrene -	„	175°–176°	„ 135°	„ : 72°	—
6. Terpinolene -	„	185°–190°	„ 116°	[„ : 50°]	—
7. Terpinene -	„	180°	—	—	155°
8. Phellandrene	„	about 170°	—	—	102°

In addition to the "Terpenes proper," $C_{10}H_{16}$, we have Hemiterpenes, C_5H_8 (see **Isoprene**), which polymerize to terpenes (dipentene); Sesqui-

terpenes, $(C_5H_8)_3$ **(Cedrene, Cardinene, Caryophyllene, and Clovene, B. Pt. 250°-260°)**; and Polyterpenes $(C_5H_8)_x$, **[Colophene, $C_{20}H_{32}$ (B. Pt. above 300°), and Caoutchouc $(C_{10}H_{16})_x$]**.

Constitution. The conception that the terpenes are dihydro-cymenes is apparently warranted in the case of many of them. The frequently observed transformation of certain terpenes into cymene (which, however, does not usually go quantitatively), and the formation of terephthalic acid by their oxidation, are in favour of this assumption. Further, carvol (*carvone*) yields oximes (*carvoximes*) which, according to *H. Goldschmidt* (B. **18**, 1733), are identical with the nitroso-limonenes prepared from limonene; carvone also yields dihydro-carveol upon reduction, and this passes into terpinene when warmed with dilute sulphuric acid (B. **24**, 3991). Again, corresponding to the (aldehyde) *citral*, $C_{10}H_{16}O$, which can yield up the elements of water and thus pass into cymene, we have as alcohol the compound *linalool*, $C_{10}H_{18}O$, which goes over into terpinene together with dipentene when water is abstracted from it (cf. *e.g.* J. pr. Ch. **45**, 596). Lastly, *A. Baeyer* has quite recently synthetized a *dihydro-cymene* which shows the terpene character in its entirety (B. **26**, 233).

Dihydro-cymenes with two ethylene linkings in the benzene nucleus can exist in various isomeric modifications according to the relative position of these linkings, being thus analogous to the dihydro-phthalic acids. Terpenes of section (*b*) probably come under this category, since their capacity for taking up four monovalent atoms is readily intelligible on the above assumption. For the terpenes of section (*a*) only one ethylene linking is to be assumed, so that their molecule perhaps contains a diagonal (*para-*) linking in addition. The side-chain may also contain the group C_3H_5 instead of C_3H_7, and therefore an ethylene- linking (terpinene?).

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1. **Pinene**, $C_{10}H_{16}$, is the chief constituent of German and American oil of turpentine, oil of juniper, of eucalyptus, of sage, etc. It forms, together with sylvestrene and dipentene, Russian and Swedish turpentine oil.

Oil of turpentine is obtained by distilling turpentine, the resin of pines, with steam, colophonium (fiddle resin) remaining behind. It is a colourless strongly refracting liquid of characteristic odour, almost insoluble in water but readily soluble in alcohol and ether. It dissolves resins and caoutchouc (being therefore used for the preparation of oil paints, lakes, etc.), also sulphur, phosphorus, etc. It absorbs oxygen from the air with the formation of ozone and production of resin,

minute quantities of formic acid, cymene, etc. being formed at the same time. Dilute nitric acid either gives rise to terephthalic acid in addition to fatty acids, or—under other conditions—to terpenylic acid, $C_8H_{12}O_4$ (which belongs to the fatty series), etc. Heating with iodine transforms it into cymene, the action being violent, and heating with hydriodic acid into the compounds $C_{10}H_{18}$ and $C_{10}H_{20}$. It acts as an antiseptic and arrests the secretions (*e.g.* that of the kidneys).

Oil of turpentine shows physical differences, according to the source from which it is derived, the German, French, and Venetian oils being lævo- and the Australian dextro-rotatory. These differences depend upon the existence of lævo- and dextro-pinenes, etc. (cf. the tartaric acids). B. Pt. 158°–161°; Sp. Gr. 0·86–0·89.

Inactive pinene can be obtained pure by heating pinene nitroso-chloride with aniline, NOCl being separated. B. Pt. 155°–156°; Sp. Gr. 0·86.

Pinene hydrochloride, $C_{10}H_{17}Cl$ (see table, p. 550), M. Pt. 125°, is a solid white crystalline mass with a camphor-like odour, whence its name of "artificial camphor," insoluble in water but readily soluble in alcohol. If its hydrochloric acid is separated by weak alkali, *e.g.* by heating it with soap, camphene is obtained (see below).

Pinene hydrochloride is incapable of further combination with HCl. From this it may be concluded that pinene has only one double bond in the molecule, and the same applies to camphene. The mono-hydriodide of pinene yields the same reduction product as bornyl iodide, viz. dihydrocamphene.

Pinene nitroso-chloride, $C_{10}H_{16}.NOCl$, results, together with cymene and pinol, by the action of ethyl nitrite, glacial acetic acid and hydrochloric acid upon pinene. Crystals; M. Pt. 103°. When heated with aniline it changes back into pure inactive pinene.

2. **Camphene**, $C_{10}H_{16}$, of which there are two modifications, dextro- and lævo-, is a solid terpene. It is obtained by heating pinene mono-hydrochloride with alcoholic potash or with dry soap, and is more stable than pinene. M. Pt. 50°.

It also results in an analogous manner from Bornyl chloride, $C_{10}H_{17}Cl$ (see Borneo camphor). It has an odour like that of oil of turpentine and camphor, and is oxidized to camphor by chromic acid mixture. With

bromine it does not yield a tetrabromide but a mono-substitution product, and it combines with only one molecule of hydrochloric acid.

3. **Fenchene**, $C_{10}H_{16}$. This is obtained from fenchone or fenchyl chloride as camphene is from camphor or bornyl chloride. It is a liquid, but is in other respects very like camphene.

4. *d*-**Limonene**, *hesperidene, citrene*, or *carvene*. The oil of the orange rind consists almost entirely of dextro-limonene, which is likewise the chief constituent of carvene, oil of dill, oil of erigeron, etc.; together with pinene it forms oil of citron. It boils at 175°, and forms a dextro-rotatory tetrabromide, $C_{10}H_{16}Br_4$, which melts at 104°, and it therefore probably contains two double linkings. The + and − tetrabromides are identical, except that their crystals are the mirror images of one another. Dextro-limonene is very easily rendered inactive, *i.e.* converted into dipentene. The "racemic" tetrabromide melts at 125°.

l-**Limonene** is present together with lævo-pinene in the oil of fir cones. Its tetrabromide has the same M. Pt. as that of the *d*-compound, viz. 104°.

l- and *d*-limonenes yield nitrosyl chlorides, $C_{10}H_{16}NOCl$, of corresponding rotatory powers; and, on the separation of hydrochloric acid from these, *l*- and *d*-**Nitroso-limonenes**, $C_{10}H_{15}NO$, which are identical with the carvoximes (p. 423).

Dihydro-dipentene, from dipentene-di-hydriodide, is exceedingly like carvo-menthene (p. 555).

4*a*. **Dipentene**, *cinene, inactive limonene*, $C_{10}H_{16}$, is found (*e.g.*) together with cineol in Oleum cinae, and is prepared by heating pinene, camphene, sylvestrene or limonene to 250°–270° for several hours, and also by the abstraction of 2HCl from its di-hydrochloride. It is further produced from pinene under the influence of dilute alcoholic sulphuric acid, from terpin hydrate and terpineol by the separation of water, by the polymerization of isoprene, and, together with the latter substance, on distilling caoutchouc. It is a liquid of pleasant odour like that of oil of citron, B. Pt. 175°–176°, and is more stable than pinene, although it can still be "isomerized" to terpinene by acids. It readily forms dipentene dihydrochloride with hydrochloric acid, and a crystalline tetrabromide with bromine, M. Pt. 125°. Its (inactive) nitroso-chloride yields, on separation of hydrochloric acid, the so-called **Nitroso-dipentene** (inactive carvoxime), M. Pt. 93°.

Dipentene di-hydrochloride, $C_{10}H_{18}Cl_2$, **crystallizes in rhombic tables, M. Pt. 50°, and is very readily soluble in hot alcohol. It is formed by the**

addition of hydrochloric acid to dipentene, limonene, etc., and also from moist pinene, this latter first undergoing conversion into its isomer, dipentene.

Terpin hydrate, $C_{10}H_{18}(OH)_2+H_2O$, is formed when the solution of dipentene di-hydrochloride in aqueous alcohol is allowed to stand, and also from pinene under the influence of alcohol and nitric acid. It crystallizes in large rhombic colourless crystals, M. Pt. 117°, which lose their water at 100°. The compound thus formed, **Terpin**, $C_{10}H_{18}(OH)_2$ (needles, M. Pt. 105°), possesses the character of glycol and yields the above dichloride again with hydrochloric acid. By the separation of H_2O it goes into **Terpineol**, $C_{10}H_{17}(OH)$, an unsaturated monatomic alcohol which is transformed by bromine into dipentene tetrabromide. Further elimination of H_2O from terpineol (by boiling it with dilute acids) gives rise to dipentene, terpinene, or terpinolene as the principal product, according to the conditions of the experiment.

5. **Silvestrene**, B. Pt. 175°, is the (dextro-rotatory) chief constituent of Swedish and Russian oil of turpentine. Its **Di-hydrochloride** is isomeric with dipentene di-hydrochloride and is dextro-rotatory. Sylvestrene is one of the most stable of the terpenes. It gives a magnificent blue colour reaction with acetic anhydride and concentrated sulphuric acid.

6. **Terpinolene**, which is very like dipentene, and:

7. **Terpinene** both result from the "isomeration" of pinene and limonene (see Terpin hydrate). Terpinene yields a nitrosite.

8. **Phellandrene**, which occurs as dextro-phellandrene in water dropwort (Phellandrium aquaticum) and as lævo-phellandrene in eucalyptus oil, yields a solid nitrosite readily with nitrous acid. Phellandrene is among the most easily altered of the terpenes; it is readily converted into dipentene, while alcoholic hydrochloric acid changes it into terpinene.

9. Synthetized **Dihydro-cymene** (see above), B. Pt. 174°. This compound, prepared from succino-succinic ester (B. **26**, 233), shows the complete terpene character, has a turpentine odour, becomes resinous on exposure to the air, decolorizes permanganate at once, and takes up bromine. It resembles the terpenes in many of its properties.

10. **Caoutchouc** $(C_{10}H_{16})_x$, is the hardened milky juice of the tropical euphorbiaceae, apocyneae, etc., especially Siphonia (ficus) elastica, which grows in Brazil, etc. It can be obtained pure, in the form of a white amorphous mass, by dissolving the crude material in chloroform and precipitating with alcohol. For its behaviour on distillation, see Dipentene. It absorbs oxygen from the air and is converted into vulcanite on treatment with sulphur.

Gutta percha (from Isonandra Gutta, which grows in India) differs from caoutchouc in that it contains oxygen.

Cantharene, C_8H_{12}, appears to be a lower homologue of the terpenes. It is obtained by acting on cantharidin with phosphorus pentasulphide, smells like turpentine, and resinifies in the air. B. Pt. 135°. When oxidized it yields *o*-toluic and phthalic acids, and is therefore probably *o*-dihydro-xylene.

The following are to be regarded as *dihydro-terpenes*:—

Menthene, $C_{10}H_{18}$, can be synthetized from menthol (p. 557) by converting it into the bromide and then splitting off hydrobromic acid. B. Pt. 167°.

Carvo-menthene, $C_{10}H_{18}$, likewise obtainable synthetically from carvone. B. Pt. 176°. Isomeric with menthene. Both these hydrocarbons are tetrahydro-cymenes (for *constitution*, see B. **26**, 824).

B. Camphors.

The most important variety of camphor is:

1. **Common or Japan Camphor**, $C_{10}H_{16}O$, which is found in the camphor tree (Laurus Camphora) and can be obtained from the latter by distillation with steam. It forms colourless transparent and readily sublimable glancing prisms of characteristic odour; M. Pt. 175°, B. Pt. 204°, Sp. Gr. 0·985. It is dextro-rotatory in alcoholic solution, the amount of rotation varying with the source of the camphor. When distilled with phosphoric anhydride it goes into cymene, zinc chloride having the same effect, though in the latter case the reaction is less simple:

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O.$$

Heated with iodine it yields carvacrol, *i.e.* oxy-cymene (p. 423), just as oil of turpentine yields cymene. Nitric acid oxidizes it to the dibasic **Camphoric acid**, $C_8H_{14}(CO_2H)_2$, which somewhat resembles phthalic acid, and which is perhaps a tetramethylene-dicarboxylic acid derivative (see B. **23**, 218, and **25**, 267, 2087; but also B. **25**, 920), and then to **Camphoronic acid**, $C_9H_{14}O_6$, etc. Camphor reacts with hydroxylamine to produce **Camphor-oxime**, $C_{10}H_{16}(NOH)$, and therefore contains a carbonyl group. The oxime can give up water and thus go into the **Cyanide**, $C_9H_{15}.CN$, which yields **Campholenic acid**, $C_9H_{15}.CO_2H$, on saponification, and **Camphylamine**, $C_9H_{15}(CH_2.NH_2)$, on reduction (B. **21**, 1125).

Camphor may be prepared artificially by oxidizing camphene (p. 552).

Two Dichlorides, $C_{10}H_{16}Cl_2$, result upon treating camphor with phosphorus pentachloride. **Chloro-**, **Bromo-**, **Nitro-**, and **Amido-camphors** are also known; likewise (*e.g.*) **Ethyl-camphor.**

Pinol, $C_{10}H_{16}O$, is an isomer of camphor which is obtained as a by-product during the preparation of pinene nitroso-chloride. B. Pt. 183°–184°. It has an odour like that of cineol, yields terebic acid on oxidation, and is indifferent to hydroxylamine. It yields a characteristic **dibromide**, $C_{10}H_{16}O.Br_2$, M. Pt. 94° (from which the bromine may be again split off), and a **hydrobromide**, $C_{10}H_{16}O.HBr$. In this latter compound the bromine may be exchanged for hydroxyl, with the formation of:

Pinol hydrate, $C_{10}H_{17}O(OH)$, a monatomic alcohol crystallizing in needles, M. Pt. 131°. It is reconverted into pinol when warmed with dilute sulphuric acid, and is oxidizable (quantitatively) to terpenylic acid, $C_8H_{12}O_4$.

Borneol or **Borneo Camphor**, $C_{10}H_{18}O$, occurs in nature (in Dryobalanops Camphora), and is produced by the action of nascent hydrogen upon Japan camphor:

$$C_{10}H_{16}O + H_2 = C_{10}H_{18}O.$$

It is very like the latter, but has at the same time an odour of pepper. It crystallizes in hexagonal plates, M. Pt. 208°, B. Pt. 212°. Oxidation converts it in the first instance into camphor.

Borneol possesses the character of a secondary alcohol, yielding compound ethers, etc., and giving with PCl_5 **Bornyl chloride**, $C_{10}H_{17}Cl$ (M. Pt. 148°), isomeric with pinene hydrochloride; bornyl chloride goes into camphene when warmed with alkalies. Borneol comports itself as a saturated compound, but at the same time it forms unstable addition-products with bromine and halogen hydride.

Cineol, *eucalyptol*, the chief constituent of Oleum cinae, and which is frequently found accompanying the terpenes, is isomeric with borneol; M. Pt. –1°, B. Pt. 176°. It is formed, among other methods, by the action of sulphuric acid upon pinene. It yields an unstable HCl-compound and readily goes into dipentene, and subsequently dipentene dihydrochloride. Oxidation converts it into the beautifully crystallizing **Cineolic acid**, $C_{10}H_{16}O_5$ (M. Pt. 196°). Acetic anhydride transforms this into **Cineolic anhydride**, $C_{10}H_{14}O_4$, which gives up carbon monoxide and carbon dioxide on being heated, with the formation of a *ketone*, $C_8H_{14}O$, apparently containing an open chain, —*methyl-hexylene ketone*. This last compound melts at 173°–

174°, and has a penetrating odour like that of amyl acetate; when heated with chloride of zinc, it passes into *m-Hydroxylol*, $C_8H_{10}.H_2$ (A. **258**, 319; **271**, 20).

1. **Terpineol**, which is also isomeric with borneol and is present in certain ethereal oils, results together with cineol from terpin, water being eliminated. M. Pt. 35°, B. Pt. 215°–218°. It behaves as a monatomic unsaturated alcohol, yields dipentene tetrabromide with bromine, and is converted into cineol by sulphuric acid. Dipentene or isomers result from terpineol by water being split off.

2. **Fenchone**, $C_{10}H_{16}O$, is present as *d*-fenchone in many fennel oils, and as *l*-fenchone in oil of Arbor vitæ; when these two are mixed, an inactive racemic compound results. It is a ketone and shows a similar behaviour to camphor; it may also be transformed into a terpene, fenchene (p. **553**), but does not yield a compound corresponding to camphoric acid.

3. **Thujone**, $C_{10}H_{18}O$, present together with *l*-fenchone in Thuja oil (oil of Arbor vitæ), possesses the properties of an unsaturated ketone. The base obtained from it by the action of ammonium formate breaks up on heating into ammonia and a hydrocarbon, $C_{10}H_{16}$, whose properties are totally different from those of the known terpenes (A. **272**, 109).

4. **Pulegone**, $C_{10}H_{16}O$ (from oil of Penny-royal), an unsaturated ketone, is isomeric with camphor (A. **272**, 122; B. **25**, 3515).

5. **Dihydro-carvone**, $C_{10}H_{16}O$, an unsaturated ketone, results upon reducing carvone, $C_{10}H_{14}O$, to the corresponding alcohol "**Dihydro-carveol**," $C_{10}H_{18}O$, and oxidizing the latter. When warmed with dilute sulphuric acid, dihydro-carveol is converted quantitatively into terpinene (B. **24**, 3984).

Tetrahydro-carvone, $C_{10}H_{18}O$, a saturated ketone, is formed by the oxidation of the corresponding alcohol "**Tetrahydro-carveol**," $C_{10}H_{20}O$, which in its turn is got by reducing dihydro-carveol. For *constitution*, see B. **26**, 824.

6. **Menthone**, $C_{10}H_{18}O$, is a saturated ketone obtained by oxidizing menthol. Liquid (B. Pt. 207°), with a soft peppermint odour. Exists in two optically different modifications (*Beckmann*, A. **250**, 322). For *constitution*, see B. **26**, 824.

Menthol, *mint-camphor*, $C_{10}H_{20}O$, is the principal constituent of oil of peppermint (Mentha piperita). It is a monatomic alcohol and forms a crystalline mass; M. Pt. 42°, B. Pt. 213°. Heated with sulphate of copper it is converted (quantitatively) into cymene. It is used as an antiseptic and anæsthetic.

Constitution of the Camphors. The compounds included in the above group are either ketones or alcohols, and—further—are either saturated or

unsaturated. The ketones can be reduced to the alcohols by treatment with sodium, while the alcohols may be reoxidized again to the ketones (A. **250**, 325). The ketones yield oximes, and can be transformed into bases by heating with ammonium formate (*Leuckart*, B. **20**, 104), *e.g.* camphor, $C_{10}H_{16}O$, into *Bornylamine*, $C_{10}H_{17}.NH_2$, a compound of characteristic behaviour (cf. B. **24**, 3993). For further details, see *e.g. Bredt*, A. **226**, 261; *Wallach*, A. **269**, 326; *Baeyer*, B. **26**, 824).

Appendix. Olefinic Camphors.

On p. 548 some unsaturated alcohols, aldehydes, and ketones of the fatty series are mentioned, which are isomeric with the camphors and very similar to these, and which can be transformed into terpenes (see p. 551; cf. *Bertram* and *Walbaum*, J. pr. Ch. **45**, 596; *Semmler*, B. **23**, 1098; **24**, 201; **25**, 1180, 3343). Among these may be mentioned:

Linalool, $C_{10}H_{18}O$, an unsaturated alcohol, is present in the oils of linaloes (German, *Linaloë*), lavender and geranium, and its acetic ether in oil of bergamot.

Citral, *geranial*, $C_{10}H_{16}O$, the aldehyde of linalool, and therefore obtainable from it by oxidation, is found in oil of citron.

Tanacetone, $C_{10}H_{16}O$, found in oil of Pansy, is a ketone.

XXXVII. RESINS; GLUCOSIDES; VEGETABLE SUBSTANCES

(of unknown constitution).

A. Resins.

Many organic compounds, the terpenes in particular, possess the property of becoming "resinified" by oxidation in the air or under the influence of chemical reagents, *i.e.* of being converted into substances very similar to the resins which occur in nature. These natural resins are solid, amorphous, and generally vitreous brittle masses of conchoidal fracture, insoluble in water and acids, but soluble in alcohol, ether and oil of turpentine. They are found naturally in abundance, partly also as balsams, *i.e.* dissolved in terpenes or ethereal oils, from which they can be separated by distilling with steam. The resins dissolve in alkalies to form compounds of the nature of soap (resin soaps), being again precipitated

from the aqueous solutions of these on the addition of acids; most resins must therefore consist of a mixture of somewhat complicated acids (the so-called resin-acids).

Abietic acid ($C_{40}H_{56}O_4$?) is an individual acid which has been isolated from colophonium (the residue from the distillation of turpentine, see below); it crystallizes in small plates, M. Pt. 165°, and is soluble in hot alcohol. **Pimaric acid,** $C_{20}H_{30}O_2$, has been prepared (*e.g.*) from galipot resin (Pinus maritima) in a similar way; M. Pt. 148°. It closely resembles abietic acid, is crystalline and forms crystalline derivatives, and exists in two modifications, dextro- and lævo-pimaric acids.

The resins show their relation to the aromatic compounds by being converted into hydrocarbons of the benzene or naphthalene series when distilled with zinc dust, and by the formation (*e.g.*) of dioxy- and trioxybenzenes when they are fused with potash.

In addition to **Colophonium,** there may be mentioned among other resins **Shellac** (from East Indian Ficus varieties), and **Amber,** a fossil resin which contains succinic acid in addition to resin-acids and a volatile oil.

The resins are largely used for the manufacture of lacs, varnishes, etc.

B. Glucosides.

(Cf. *O. Jacobsen's* "Die Glucoside," Breslau, *Trewendt.*)

As glucosides are designated a series of vegetable substances which are so broken up by alkalies, acids, or enzymes, that one of the products of this decomposition is a glucose, usually grape sugar. They are thus ethereal derivatives of the sugar varieties in question. Some of them have been mentioned already.

Amygdalin, $C_{20}H_{27}NO_{11}$ (p. 433), is found in bitter almonds, in the leaves of the cherry laurel, in the kernels of the peach, cherry and other amygdalaceae. It crystallizes in colourless prisms, M. Pt. 200°, is readily soluble in water, and breaks up

into oil of bitter almonds, dextrose and hydrocyanic acid under the influence of emulsin (p. 322), or when saponified.

Among others there may be mentioned:

Salicin, $C_{13}H_{18}O_7$, found in varieties of Salix, which breaks up into saligenin (*o*-oxy-benzyl alcohol) and dextrose; **Helicin**, $C_{13}H_{16}O_7 + H_2O$, which results from the action of N_2O_3 upon salicin and is decomposable into salicylic aldehyde and glucose, from which it can again be obtained synthetically; **Populin** or *benzoyl-salicin*, $C_{20}H_{22}O_8$ (in varieties of Populus), which can be prepared artificially from benzoyl chloride and salicin.

Arbutin, $C_{12}H_{16}O_7$, and **Methyl-arbutin**, $C_{13}H_{18}O_7$, present in the leaves of the bear-berry, etc., break up into glucose and hydroquinone or methyl-hydroquinone respectively. Arbutin is used in medicine.

Hesperidin, $C_{22}H_{26}O_{12}$, which is contained in unripe oranges, etc., can be decomposed into glucose, hesperetic acid (isomeric with ferulic acid, p. 463), and phloroglucin.

Phloridzin, $C_{21}H_{24}O_{10}$ (fine prisms), found in the bark of fruit trees, can be split up into grape sugar and **Phloretin**, $C_{15}H_{14}O_5$, and this latter—in its turn—into phloretic acid and phloroglucin (p. 426). Both induce glycosuria (*i.e.* a functional derangement of the liver, giving rise to temporary diabetes) in animals.

Aesculin, $C_{15}H_{16}O_9$ (prisms), present in the bark of the horse-chestnut, is decomposed by acids into grape sugar and Aesculetin (dioxy-cumarin, p. 464), $C_9H_{16}O_4$.

Saponin, $C_{32}H_{52}O_{17}$ (in the soapwort).

Digitonin, $C_{27}H_{46}O_{14}$, **Digitalin**, $C_{29}H_{46}O_{12}$, and **Digitaleïn**, are three glucosides which, together with *digitoxin*, $C_{21}H_{32}O_7$ (the most important constituent from a pharmacological point of view), are present in the digitalis of commerce (cf. B. **24**, 339; **25**, Ref. 680).

Quercitrin, $C_{36}H_{38}O_{20}$, found in Quercus tinctoria, chestnut blossoms, etc.; yellow needles.

Coniferin, $C_{16}H_{22}O_8 + 2H_2O$ (in the cambium sap of the coniferae), breaks up into glucose and coniferyl alcohol, and serves for the preparation of vanillin, which results from it upon oxidation (p. 437).

Myronic acid, $C_{10}H_{19}O_{10}NS_2$, is present as potassium salt, $C_{10}H_{18}KO_{10}NS_2$ (glancing needles), in black mustard seed. It is broken up into grape sugar, potassium bisulphate and allyl isothiocyanate by baryta water or by the enzyme Myrosin, which likewise occurs in the mustard seed.

Ruberythric acid, see p. 513.

For *synthetized glucosides*, see B. **18**, 1960, 3481.

C. Vegetable substances of unknown Constitution.

Aloïn, $C_{17}H_{18}O_7$ (in the aloe plant), crystallizes in fine needles and is a powerful purgative: it is a derivative of anthracene.

Cantharidin, $C_{10}H_{12}O_4$ (in Spanish fly), forms sublimable plates; it blisters the skin.

Picrotoxin, $C_{30}H_{34}O_{13}$ (in the seeds of Cocculus indicus).

Santonin, $C_{15}H_{18}O_3$ (in worm seed), is derived from naphthalene (B. **16**, 2686; **24**, Ref. 908).

Among natural dyes of unknown constitution we have:

Brasilin, $C_{16}H_{14}O_5$, the red dye of Brazil and Fernambuco woods. Colourless glancing needles; it appears to be a derivative of resorcin (B. **25**, 18).

Curcumin, $C_{14}H_{14}O_4$?, the yellow dye of the turmeric root, is turned brownish-red by alkalies, for which it forms a delicate test.

Hæmatoxylin, $C_{16}H_{14}O_6$, is the colouring matter of logwood (Hæmatoxylon Campechianum). It forms yellowish prisms, which dissolve in alkalies with a violet-blue colour.

Carminic acid, $C_{17}H_{18}O_{10}$, the active principle of cochineal (Coccus Cacti), is a red amorphous mass which is split up by acids into a sugar (not glucose) and **Carmine red,** $C_{11}H_{12}O_7$, the latter forming a purple-red mass with a green reflection; bromine converts carminic acid into a dibromo-derivative of a methylated and hydroxylated phthalic acid (B. **18**, 3180).

Harmin, $C_{13}H_{12}N_2O$, and **Harmalin,** $C_{13}H_{14}N_2O$, are the colouring matters of Peganum Harmala (B. **18**, 400).

Chlorophyll or *leaf green*, is the green colouring matter of plants, and contains iron in its molecule. Together with starch, wax, etc., it forms the chlorophyll granules of the cells, but, notwithstanding that it has been the subject of numerous investigations, its nature is not yet accurately known.

Litmus is a blue dye obtained from Roccella tinctoria and other lichens; it is related to orceïn (p. 425), and is turned red by acids, the blue colour being restored by alkalies. Hence it is much used as an indicator in alkalimetry.

XXXVIII. ALBUMINOUS SUBSTANCES; ANIMAL CHEMISTRY.

An extended description of the substances (other than those already mentioned) which are found in the animal organism and which are therefore of importance for physiological chemistry, will not be attempted here, since they are for the most part better known from a physiological than from a chemical point

of view. Only the albumens and albuminoids, both of which are classed as proteids, and some of the substances which are produced during metabolic processes, will be treated of.

A. Albumens.

(Cf. *Drechsel's* article "Eiweiss" in *Ladenburg's* Neues Handwörterbuch.)

The albumens make up the chief part of the organism, being present partly in the soluble and partly in the solid state; they are found in protoplasm and in all the nutritive fluids of the body. In solution they are opalescent, optically (–) active, and do not diffuse through parchment paper, *i.e.* are colloids; but they are thrown down when the solution is warmed, or upon the addition of strong mineral acids, of many metallic salts [*e.g.* copper sulphate, basic lead acetate and mercuric chloride], of alcohol, tannic acid, acetic acid together with a little potassium ferrocyanide, etc. When boiled: (*a*) with nitric acid, they are coloured yellow (the xantho-proteïn reaction); (*b*) with a solution of mercuric nitrate containing N_2O_3 (*Millon's reagent*), red; (*c*) with caustic soda solution and a very little cupric sulphate, violet. The albumens combine both with acids and alkalies to acid- and alkali-albuminates (see below).

Many of the albumens have been prepared pure, although this is a very difficult operation. With the exception of the crystalline albumen which occurs in hemp, castor oil, and pumpkin seeds (B. 15, 953), and the recently isolated crystalline egg albumen (B. 24, Ref. 469; 25, Ref. 173), they do not crystallize.

The different albumens vary only slightly among themselves in percentage composition; they contain:

$$C = 52{\cdot}7 \text{ to } 54{\cdot}5 \text{ p.c.}; \; H = 6{\cdot}9 \text{ to } 7{\cdot}3 \text{ p.c.}; \; N = 15{\cdot}4 \text{ to } 16{\cdot}5 \text{ p.c.};$$
$$O = 20{\cdot}9 \text{ to } 23{\cdot}5 \text{ p.c.; and } S = 0{\cdot}8 \text{ to } 2{\cdot}0 \text{ p.c.}$$

It is impossible at present to construct a formula from these numbers.

The fact that albumen contains sulphur is worthy of note, though the mode in which it is combined in the molecule is unknown; warming with a dilute alkaline solution is sufficient

to eliminate it partially, *e.g.* when white of egg is boiled with an alkaline solution of lead oxide, sulphide of lead is separated (the test for sulphur in albumen).

Albumen preparations usually leave a very considerable amount of ash, *i.e.* inorganic salts, on incineration. It is not yet certain in how far this mineral matter forms an integral constituent of these substances; but the properties of "egg albumen free from ash" are materially different from those of ordinary albumen (B. **25**, 204).

Constitution. The way in which albumen is split up by acids (especially in presence of stannous chloride), or by baryta water, gives some indication of its constitution. Here, in addition to ammonia and carbonic acid, amino-acids are the principal products, and these belong not only to the fatty series [*e.g.* glycocoll, leucine, aspartic acid, glutamic acid and "leuceïn," $(C_4H_7NO_2)_x$ (B. **19**, Ref. 30), "lysine," $C_6H_{14}N_2O_2$ (probably di-amino-caproic acid, B. **25**, 3504)], but also to the aromatic (*e.g.* phenyl-amino-propionic acid and tyrosine).

Loew's hypothesis that albumen is essentially a condensation product of aspartic aldehyde, $C_4H_7NO_2$, *i.e.* of leuceïn, is worthy of mention.

The putrefaction of albumen gives rise not only to amino-acids but also to other aromatic and fatty acids (*e.g.* butyric acid), indole, skatole, and cresol; further, to the alkaloid-like **Ptomaïnes** (the toxines or poisonous alkaloids produced in dead bodies), of which neurine and pentamethylene-diamine (or "Cadaverin," B. **19**, 2585) have been isolated (cf. p. 211). For a compilation of the ptomaïnes, see *Brieger*, Archiv. f. patholog. Anatomie, **115**, 483.

Albuminous matters undergo change when acted upon by the juices of the stomach at a temperature of 30°–40°, pepsin converting them in the first instance into **Anti-** and **Hemi-albumoses**, both of which then pass into peptone; trypsin, the enzyme of the pancreas, likewise gives rise to the two above albumoses, but then transforms the anti-compound into peptone and the hemi-compound into leucine, tyrosine, aspartic acid and glutamic acid (the pancreatic digestion; for details, see *Kühne*, B. **17**, Ref. 79). The peptones are readily soluble in water, diffuse quickly through vegetable parchment, and they are neither coagulated upon heating nor by most of the reagents which coagulate albumen, *e.g.* sulphate of ammonium.

The albumoses are thrown down by ammonium sulphate.

When soluble salts of iron are allowed to act upon white of egg and upon peptone, **Iron albuminate** and **Iron peptonate** are respectively produced, these being employed in medicine as iron preparations for internal use under the names of *liquor ferri albuminati* and *peptonati*.

Classification of the albumens.

1. *Coagulable albumens:*

A. Those which are soluble in water and not precipitable by common salt, but which become insoluble, *i.e.* coagulate, when the solution is heated to 70°–75°; to this class belong **Egg albumen** (in the white of birds' eggs), **Serum albumen** (the chief constituent of all nutritive fluids, of the blood, chyle, etc.), and **Phyto-albumen** (in plants).

B. Those which are insoluble in water, but soluble in a dilute solution of common salt, being thrown down however by an excess of the latter, and which coagulate upon warming (fibrinogene at 56°, and the others at 70°–75°). These include the *globulines*, viz. **Globuline** (in the crystalline lens of the eye), **Fibrinogene** or *meta-globuline* (in blood, chyle, etc.), **Para-globuline** (in blood), and **Phyto-globuline** (in plants). **Vitellin** (in the yolk of egg) is related to the last-named, but is not precipitable by common salt.

2. *Coagulated albumens*, etc. Insoluble in water:

A. **Coagulated albumens**: **Fibrin** (an essential constituent of clotted blood, which separates at once when the blood leaves the organism), **Myosin** (which separates from the plasma of living muscle), and **Phyto-myosin** (the coagulated albumen of flour paste). The two last dissolve in a 10 per cent solution of common salt, and coagulate in this solution at 56°–57°.

B. **Coagulates.** In this class we have **Syntonin** or *acid albumen*, which is insoluble in a solution of common salt, but readily soluble in dilute acids or alkalies, from which it is thrown down on neutralization, but not by heat.

C. **Alkali albuminate.** Soluble in alkali and precipitable from this solution by acid; insoluble in water and in solutions of salts.

The **Legumin** of plants perhaps belongs to this class.

3. *Compound albumens* (*Nucleo-albumens*):

A. **Caseins.** These are found in milk only. They are insoluble in water and in a solution of sodium chloride, but readily soluble in dilute hydrochloric acid or carbonate of potash; they are not thrown down from solution upon boiling. Caseïn is kept in solution in milk by alkali, is separated on the addition of acid, and is coagulated by the addition of rennet (an infusion of the stomach of the calf) as a sparingly soluble cheese.

B. **Nucleo-albumens** (see under "Nucleïns").

C. **Hæmoglobins.** **Hæmoglobin** is the colouring matter of the red blood corpuscles. It can be broken up into albumen and hæmatin (see below).

Hæmoglobin combines very readily with oxygen, *e.g.* in the lungs, to **Oxyhæmoglobin**, which yields up its oxygen again, not only in the organism but also in a vacuum and when exposed to the action of reducing agents. With carbon monoxide it combines to the compound, **Carbon monoxide-hæmoglobin**. All three compounds can be obtained crystallized in the cold, and they possess characteristic absorption-spectra. **Hæmatin** ($C_{32}H_{32}N_4FeO_4$?), a dark brown powder containing 8 p.c. of iron, results even from the spontaneous decomposition of hæmoglobin. Its hydrochloride, **Hæmin** ($C_{32}H_{30}N_4FeO_3$, HCl?), is obtained in the form of characteristic microscopic, reddish-brown crystals by the action of glacial acetic acid and some common salt upon oxy-hæmoglobin; this is a delicate test for the presence of blood.

Nucleïns. The nucleïns are important constituents of the cell nucleus, *e.g.* of pus cells, of nucleated blood corpuscles, of yeast cells, etc. They form white masses insoluble in water or dilute mineral acids but readily soluble in alkalies, and contain phosphoric acid in ethereal combination. Some of them, the nucleo-albumens, break up when boiled with water or dilute acids into albumen, hypoxanthine and the acid just named. Certain varieties of nucleïn are free from sulphur while others contain it, the latter yielding tyrosine when decomposed. The product which is obtained when the albumen of hens' eggs is coagulated by *m*-phosphoric acid resembles nucleïn.

B. Albuminoids.

The albuminoids are to be regarded as the nearest derivatives of the albumens, being closely related to these; they are mostly organized, and are important constituents of the tissue. Some of them are converted into glue when boiled with water, and hence are termed glue-yielding substances. They give "bone oil" (p. 519) on destructive distillation.

To this group belong:

1. **Glutin or Bone glue**, known as gelatine in the pure state, which is characterized by its solution solidifying to a jelly on cooling; it is obtained by boiling bone cartilage, connective tissue, stag's horn, calves' feet, etc. (the so-called "collogenes") with water.

Unlike the albumens, glutin is not precipitated from aqueous solution by nitric acid or potassium ferrocyanide. Tannic acid throws down gelatine from solution, and unites with the glue-yielding substances of the organism to form compounds insoluble in water (the tanning of hide; leather). For glutin-peptone salts, see B. **25**, 1202.

Bone glue yields glycocoll and leucine when boiled with acids, but no tyrosine.

2. **Mucin** or **Mucus**, found in slime secretions, is free from sulphur.

3. **Keratin** or *horn substance* goes to build up the epidermis, nails, hair, etc.; it contains sulphur. Is not attacked by the gastric juice.

4. **Elastin** is the chief constituent of the elastic ligaments of the organism. It does not contain sulphur, and yields leucine with sulphuric acid.

5. The enzymes (*unorganized ferments*) diastase, ptyalin, pepsin, trypsin, etc., already mentioned at p. 322, also belong to this group.

6. **Chitin**, the principal constituent of the cuticular covering of the articulata, *e.g.* of the shell of the crab, differs from horn substance in being insoluble in alkalies; it yields glucosamine (p. 312) when boiled with acids (B. 17, 241).

D. Substances produced during Metabolic processes.

1. *Acids of the bile.* Bile contains the sodium salts of **Glycocholic acid**, $C_{26}H_{43}NO_6$, and **Taurocholic acid**, $C_{26}H_{45}NSO_7$, both of which are decomposed by alkalies into **Cholic acid**, $C_{24}H_{40}O_5$, $= C_{21}H_{32}(OH)(CO_2H)(CH_2.OH)_2$, on the one hand, and glycocoll and taurine respectively on the other.

2. The bile also contains various colouring matters: **Bilirubin, Biliverdin, Bilifuscin**, etc. These apparently bear some simple relation to the colouring matter of blood, the formula of bilirubin being $C_{32}H_{36}N_4O_6$ (see B. 17. 2267).

3. The **Cholesterins**, $C_{26}H_{43}(OH)$, of which numerous varieties are now known, are present in blood, bile, nerve substance, vegetable fats, etc. They are monatomic alcohols, and crystallize in small plates with a mother-of-pearl lustre.

4. **Lanolin** or *wool fat* consists of fatty esters of cholesterin. It is a valuable salve, and is distinguished from other fats by the readiness with which it is absorbed into the skin and by its power of taking up water.

5. **Cerebrin**, $C_{17}H_{33}NO_3$, is an important ingredient of the medullary substance of the nerve.

6. **Lecithin**, $C_{42}H_{84}NO_9P$, is a characteristic constituent of nerve substance, brain, yolk of egg, etc. It forms a waxy mass capable of crystallization, which dissolves in alcohol and ether, and swells up to an opalescent liquid with water. It breaks up on saponification into choline, glycerine-phosphoric acid, stearic and palmitic acids, and is therefore to be regarded as glycerine in which the three hydroxyl hydrogens have been replaced by the palmitic, stearic and phosphoric acid residues, the last of which still remains in ethereal combination with choline.

APPENDIX A. (to p. 475).

Cumarone and Indazole Groups.

Just as furfurane and thiophene are related to pyrrol, so there are compounds analogous to indole which contain oxygen or sulphur in place of the imido-group.

Cumarone, $C_6H_4<^{O}_{CH}>CH$, is a compound which closely resembles the benzene hydrocarbons, especially pseudo-cumene; it is found in coal tar, from which it can be isolated by means of its compound with picric acid. It is a liquid of very negative properties (B. Pt. 170°–171°), being resinified however by mineral acids, with the production of a red colour. When its vapour, mixed with that of benzene (or naphthalene), is led through a red-hot tube, phenanthrene (or chrysene) is produced. Cf. B. **23**, 78; **25**, 2409. For analogous compounds, see B. **19**, 1290, 1432, 1617, 1667, and 2927.

There exist still other compounds, the *Indazoles*, derived from the indoles, but differing from these in that they contain a nitrogen atom instead of a nucleus-carbon atom. Corresponding to indole we have **Indazole,** $C_7H_6N_2$, $= C_6H_4<^{N}_{CH}>NH$ or $C_6H_4<^{NH}_{CH}>N$, a weak base, which can be prepared indirectly from *p*-nitro-*o*-toluidine by transforming this into the diazo-compound, boiling the latter with glacial acetic acid, and then eliminating the nitro-group (B. **23**, 3635; **24**, 2370; **25**, 3149; **26**, 216, etc.).

APPENDIX B. (to p. 504, after line 30).

The two **Naphthalene-mono-sulphonic acids,** $C_{10}H_7(SO_3H)$, are formed when naphthalene is warmed with concentrated sulphuric acid, and are crystalline hygroscopic compounds; the α-acid undergoes a molecular transformation into the β- when heated with sulphuric acid. They yield the two naphthols on fusion with alkalies, and the two **Cyano-naphthalenes,** $C_{10}H_7.CN$ (crystalline compounds which can be distilled without decomposition), when heated with cyanide of potassium.

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